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Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options Volume XVII. Nitrogen Oxides Summary Report

Arthur D. Little, Inc., Cambridge, MA

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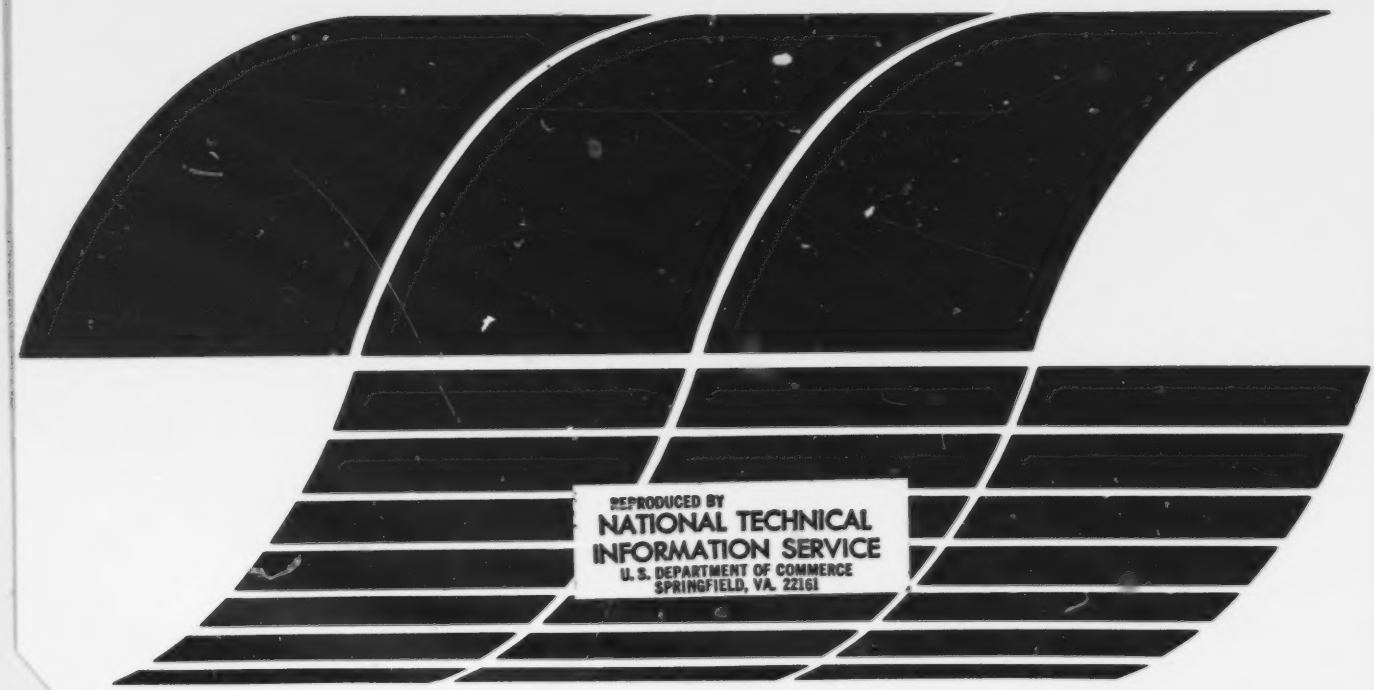
Volume XVII
Nitrogen Oxides Summary Report

Interagency Energy/Environment R&D Program Report



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This present report summarizes the information regarding nitrogen oxide pollutants in the 13 industry reports. Four parallel reports treat sulfur oxides, particulates, solid residues, and toxics/organics. All of these pollutant oriented reports are intended to be closely used with the original 15 reports.

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ENVIRONMENTAL CONSIDERATIONS OF SELECTED ENERGY-CONSERVING MANUFACTURING PROCESS OPTIONS

Volume XVII. Nitrogen Oxides Summary Report

by

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Contract No. 68-03-2198

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment, and even on our health, often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report summarizes information on nitrogen oxides from a study of 13 energy-intensive industries. If implemented over the coming 10 to 15 years, these processes and practices could result in more effective utilization of energy resources. The study was carried out to assess the potential environmental/energy impacts of such changes and the adequacy of existing control technology in order to identify potential conflicts with environmental regulations and to alert the Agency to areas where its activities and policies could influence the future choice of alternatives.

The results will be used by the EPA's Office of Research and Development to define those areas where existing pollution control technology suffices, where current and anticipated programs adequately address the areas identified by the contractor, and where selected program reorientation seems necessary.

Specific data will also be of considerable value to individual researchers as industry background and in decision-making concerning project selection and direction.

The Power Technology and Conservation Branch of the Energy Systems-Environmental Control Division should be contacted for additional information on the program.

David G. Stephan
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Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Under EPA Contract No. 68-03-2198, Arthur D. Little, Inc. undertook a study of the "Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options." Some 80 industrial process options were examined in 13 industrial sectors. Results were published in 15 volumes, including a summary, industry prioritization report, and 13 industry oriented reports (EPA-600/7-76-034 a through o).

This present report summarizes the information regarding solid residues in the 13 industry reports. Four parallel reports treat sulfur oxides, nitrogen oxides, particulates, and toxics/organics. All of these pollutant-oriented reports are intended to be closely used with the original 15 reports.

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ENGLISH-METRIC (SI) CONVERSION FACTORS

To Convert From	To	Multiply By
Acre	$Metre^2$	4,046
Atmosphere (normal)	Pascal	101,325
Barrel (42 gal)	$Metre^3$	0.1589
British Thermal Unit	Joule	1,055
Centipoise	Pascal-second	0.001
Degree Fahrenheit	Degree Celsius	$t_C^o = (t_F^o - 32)/1.8$
Degree Rankine	Degree Kelvin	$t_K^o = t_R^o/1.8$
Foot	Metre	0.3048
$Foot^3$/minute	$Metre^3$/sec	0.0004719
$Foot^3$	$Metre^3$	0.02831
$Foot^2$	$Metre^2$	0.09290
Foot/sec	Metre/sec	0.3048
$Foot^2$/hr	$Metre^2$/sec	0.00002580
Gallon (U.S. liquid)	$Metre^3$	0.003785
Horsepower (550 ft-lbf/sec)	Watt	745.7
Horsepower (electric)	Watt	746.0
Horsepower (metric)	Watt	735.5
Inch	Metre	0.02540
Kilowatt-hour	Joule	3.60×10^6
Litre	$Metre^3$	1.000×10^{-3}
Micron	Metre	1.000×10^{-6}
Mil	Metre	0.00002540
Mile (U.S. statute)	Metre	1,609
Poise	Pascal-second	0.1000
Pound force (avdp)	Newton	4.448
Pound mass (avdp)	Kilogram	0.4536
Ton (Assay)	Kilogram	0.02916
Ton (long)	Kilogram	1,016
Ton (metric)	Kilogram	1,000
Ton (short)	Kilogram	907.1
Tonne	Kilogram	1,000

Source: American National Standards Institute, "Standard Metric Practice Guide," March 15, 1973. (ANS72101-1973) (ASTM Designation E380-72)

SECTION I

INTRODUCTION

BACKGROUND AND PURPOSE

During 1975 and the first half of 1976, under EPR Contract No. 68-03-2198, Arthur D. Little, Inc., undertook a study of the "Environmental Considerations of Selected Energy-Conserving Manufacturing Process Options" in 13 energy-intensive industry sectors for the U.S. Environmental Protection Agency (EPA). The results of these studies were published in the following reports:

- Volume I -- Industry Summary Report (EPA-600/7-76-034a)
- Volume II -- Industry Priority Report (EPA-600/7-76-034b)
- Volume III -- Iron and Steel Industry (EPA-600/7-76-034c)
- Volume IV -- Petroleum Refining Industry (EPA-600/7-76-034d)
- Volume V -- Pulp and Paper Industry (EPA-600/7-76-034e)
- Volume VI -- Olefins Industry (EPA-600/7-76-034f)
- Volume VII -- Ammonia Industry (EPA-600/7-76-034g)
- Volume VIII -- Alumina/Aluminum Industry (EPA-600/7076-034h)
- Volume IX -- Textiles Industry (EPA-600/7-76-034i)
- Volume X -- Cement Industry (EPA-600/7-76-034j)
- Volume XI -- Glass Industry (EPA-600/7-76-034k)
- Volume XII -- Chlor-Alkali Industry (EPA-600/7-76-034l)
- Volume XIII -- Phosphorus/Phosphoric Acid Industry (EPA-600/7-76-034m)
- Volume XIV -- Copper Industry (EPA-600/7-76-034n)
- Volume XV -- Fertilizer Industry (EPA-600/7-76-034o)

In the course of this study, some 80 industrial process options were examined, focusing on:

- Identification of any major sources and amounts of pollutants (air, water and solid) expected from the processes,
- Development of estimated capital and operating costs for both production and pollution control aspects of the processes,
- Estimation of the types and amounts of energy used in both production and pollution control for the processes,
- Assessment of the economic viability and likelihood of implementation of those alternative process options being studied,
- Identification of areas where EPA's activities and policies could influence the future choice of alternatives, and
- Identification of research and development areas in both process and pollution control technology.

Because of the industry orientation of the study (encompassing 15 volumes and some 1,700 pages), it was felt that pollutant-specific information across all the 13 sectors studied should be summarized. Five such pollutants were identified to be of particular interest:

- Nitrogen oxide (NO_x) emissions,
- Sulfur oxide (SO_x) emissions,
- Fine particulate emissions,
- Solid residues, and
- Organic and/or toxic pollutants.

A summary pollutant report in each of these areas has been prepared. Although we did attempt some estimates and extrapolations on pollutants where information was readily available, in general, we did not attempt to go beyond the contents of the 15 original reports.

APPROACH

These summary pollutant reports are intended to be used closely with the original 15 reports. Generally, information, such as detailed descriptions of the processes, has not been duplicated in these pollutant reports. Sections of the previous 15 reports in which this information can be found have been extensively referenced by volume number and page number (e.g., Volume VII, page 20, refers to page 20 of the Ammonia Industry report).

In Section 2 of this report (Findings and R&D Overview), summary information on generic, cross-industry problems that emerge and suggestions for research and development work in the areas of both pollution control technology and process technology are presented. In Section 3 of this report, availability and applicability of NO_x pollution control technology are presented, and NO_x emissions and controls reported in our previous study are summarized. Unless otherwise noted, the factional percent of NO_x in gas streams is reported as NO_2 equivalent. All emissions are estimated unless specifically referenced, since we believe that actual data do not exist for many of the processes described, which are frequently still under development.

To give the reader a sense of the size of the industries for which the pollution problems covered in these summary pollutant reports are considered, Table 1 lists these industries, their total production in 1974 (the baseline year for the study), and their projected incremental production in 1989 -- 15 years hence.

TABLE 1. PROJECTED U.S. PRODUCTION IN INDUSTRIES STUDIED

Commodity	Total U.S. projection in 1974 (10^6 tons*)	Projected rate of growth (%/yr)	Total projected production in 1989 (10^6 tons)	Increase in annual production in 1989 over that of 1974 (10^6 tons)
Alumina	7.7	6.0	18.5	10.75
Aluminum	5.0	6.0	12.0	7.0
Ammonia	9.2	6.0	22.0	12.8
Cement	79.0	2.0	106.3	27.3
Chlorine	11.0	5.0	22.9	11.9
Coke	62.0	2.5	89.8	27.8
Copper	1.6	3.5	2.7	1.1
Fertilizers (HNO_3)	8.2	4.0	14.8	6.6
Glass (flat)	29.0	2.5	42.0	13.0
Iron	100.0	2.5	144.8	44.8
Olefins (ethylene)	13.0	8.0	41.2	28.2
Petroleum	740.0**	1.5	925.0***	185.0****
Pulp (Kraft)	16.0	5.0	33.3	17.3
Pulp (newsprint)	3.9	2.5	5.6	1.7
Phosphoric Acid (detergent grade)	1.4	2.5	2.03	0.63
Phosphoric Acid (wet acid grade)	9.0	2.5	13.0	4.0
Steel	133.0	2.5	193.0	60.0
Textiles (knit)	0.32	2.2	0.44	0.12
Textiles (woven)	2.1	2.2	2.91	0.81

*All tons referred to in these reports are net tons, unless otherwise indicated.
**Approximate equivalent of 30 quads (1 quad is equal to 10^{15} Btu).
***Approximate equivalent of 37.5 quads.
****Approximate equivalent of 7.5 quads.

SECTION 2

FINDINGS AND R&D OVERVIEW

FINDINGS

Seven of the 13 industries addressed in the original study have process-related NO_x pollution problems and are therefore covered in this report. These industries are alumina/aluminum, cement, copper, fertilizers, flat glass, olefins, and petroleum refining. Industries which do not have NO_x emission problems or industries in which the emissions are not altered by the process change are not included here because these process changes are not important from the point of view of NO_x emissions. Table 2 presents a summary of the estimated NO_x emissions from both the base case processes and process alternatives in these seven industries.

The emission factors shown in the table include both process and power boiler emissions. Emissions from the power boilers were generally not estimated in the original study but are included here because emissions from the base case and alternative processes are compared in this report by considering the total system. The power boilers include on-site power boilers for steam and electricity generation and utility power boilers (off-site power plants) for electricity generation. The emission factors vary in the range of 3.0 to 15.0 lb/ton of product. The exceptions are:

- Processes in the aluminum industry which have high emissions due to consumption of large quantities of electricity;
- The nitric acid industry without NO_x control which has high emissions (emission factor 52.0 lb of NO_x/ton of acid);
- The nitric acid industry with NO_x emissions controlled catalytically using hydrogen or molecular sieve methods which has low emissions (0.1 to 1.1 lb of NO_x/ton of acid); and
- Processes in which combustion is controlled and therefore emissions are low, such as the fluidized bed process in place of a kiln in the cement industry (emission factor 0.65 lb of NO_x/ton of cement).

As is shown in Table, the greatest volume of NO_x emissions from base case processes in the year 1974 was estimated to come from petroleum refining operations, followed by aluminum, fertilizers, cement, flat glass, etc. Table 2 also shows estimated incremental NO_x emissions (1989 - 1974) based on the increase in production from 1974 to 1989 as determined from Table 1. Incremental emissions are shown from both the base case and alternative processes assuming dedication of 100% of the incremental production rather than a fraction to each process (base case and alternative).

TABLE 2. SUMMARY OF ESTIMATED ANNUAL NO_x EMISSIONS

Commodity	Process	NO_x emissions in 1974 from base case process (10^6 lb/yr)	Incremental NO_x emissions 1989-1974 (10^6 lb/yr)	Change from base case in 1989 (10^6 lb/yr)
Petroleum	Base case: East Coast refinery	1,244	311	-
	• Direct combustion of asphalt in process heaters and boilers	--	373	+ 62
	• Flexicoking	--	311	0
	Base case: Gulf Coast refinery	1,343	336	-
	• On-site electric power by combustion of vacuum bottoms	--	319	- 17
	Base case: West Coast refinery	(b)	(b)	-
	• Hydrocracking of heavy bottoms	(b)	(b)	0
	• High-purity hydrogen via partial oxidation of asphalt	(b)	(b)	0

(continued)

TABLE 2. (continued)

Commodity	Process	NO_x emissions in 1974 from base case process (10^6 lb/yr)	Incremental NO_x emissions 1989-1974 (10^6 lb/yr)	Change from base case in 1989 (10^6 lb/yr)
Olefins	Base case: Ethane-propane process	169	389	-
	• Naphtha process	--	358	- 31
	• Gas-oil process	--	369	- 20
Cement	Base case: Long dry kiln	300	104	-
	• Suspension preheater	--	82	- 22
	• Flash calciner	--	82	- 22
	• Fluidized bed	--	18	- 86
	• Coal as fuel instead of gas or oil in long dry kiln	--	104	0
Alumina	Base case: Bayer process	72.9	102	-
	• Hydrochloric acid ion exchange	--	267	+165
	• Nitric acid ion exchange	--	108	+ 6
	• Toth alumina	--	90	- 12

(continued)

TABLE 2. (continued)

Commodity	Process	NO_x emissions in 1974 from base case process (10^6 lb/yr)	Incremental NO_x emissions 1989-1974 (10^6 lb/yr)	Change from base case in 1989 (10^6 lb/yr)
Aluminum	Base case: Hall-Heroult (current practice, C.P.)	628	879	-
	• Hall-Heroult (new)	--	680	- 199
	• Alcoa chloride	--	592	- 287
	• Refractory hard metal cathode	--	705	- 174
	Base case: Bayer with Hall-Heroult (C.P.)	701	1,007	
	• Clay chlorination (Toth Alumina) and alcoa chloride	--	664	- 343
Flat Glass	Base case: Natural gas firing	236	106	-
	• Coal gasification	--	116	+ 10
	• Direct coal firing	--	132	+ 26
	• Coal-fired hot gas generation	--	148	+ 42

(continued)

TABLE 2. (continued)

Commodity	Process	NO_x emissions in 1974 from base case process (10^6 lb/yr)	Incremental NO_x emissions 1989-1974 (10^6 lb/yr)	Change from base case in 1989 (10^6 lb/yr)
Flat Glass (cont.)	• Electric melting	--	93	- 13
	• Batch preheating with natural gas firing	--	85	- 21
Copper	Base case: Conventional smelting	19.4	13	-
	• Outokumpu flash smelting	--	.9	- 4
	• Noranda	--	6	- 7
	• Mitsubishi	--	5 ± 2	- 8
	• Arbiter	--	34	+ 21
Fertilizers (Nitric acid)	Base case: Uncontrolled*	426	343	-
	• Catalytic reduction	--	--	-
	• Natural gas fired	--	27	- 316
	• Hydrogen fired	--	.7	- 342
	• 75% Hydrogen/25% natural gas	--	.7	- 342

(continued)

TABLE 2. (continued)

Commodity	Process	NO_x emissions in 1974 from base case process (10^6 lb/yr)	Incremental NO_x emissions 1989-1974 (10^6 lb/yr)	Change from base case in 1989 (10^6 lb/yr)
Fertilizers (cont.)	• Molecular sieve	--	7.3	- 336
	• Grande Paroisse	--	24	- 319
	• CDL/Vitok	--	21	- 322
	• Masar	--	17	- 326
Ammonia	Base case: Ammonia via natural gas	91	127	-
	• Ammonia via coal gasification	--	344	+ 217
	• Ammonia via heavy fuel oil	--	155	+ 28
Iron and Steel	Base case: No off gas recovery	30	22	-
	• Off gas recovery	--	11	- 11
	Base case: Blast furnace	7	3.1	-
	• Blast furnace with external desulfurization	--	3.1	-
	Base case: Wet quenching of coke	(a)	(a)	-

(continued)

TABLE 2. (continued)

Commodity	Process	NO_x emissions in 1974 from base case process (10^6 lb/yr)	Incremental NO_x emissions 1989-1974 (10^6 lb/yr)	Change from base case in 1989 (10^6 lb/yr)
Iron and steel (cont.)	• Dry quenching of coke	--	- 21	- 21
	Base case: Steelmaking coke oven, blast furnace, BOP route	148	108	-
	• Direct reduction, EAF route	--	336	+ 228
Phosphorus/ phosphoric acid	Base case: Electric furnace	67	30.1	-
	• Chemical cleanup of wet-process acid	--	2.9	- 27
	• Solvent extraction of wet-process acid	--	4.2	- 26
Textiles	Knit fabric:			
	• Base case: Conventional aqueous	2.5	.95	-
	• Advanced aqueous	--	.65	- .30
	• Solvent processing	--	.34	- .61

(continued)

TABLE 2. (continued)

Commodity	Process	NO_x emissions in 1974 from base case process (10^6 lb/yr)	Incremental NO_x emissions 1989-1974 (10^6 lb/yr)	Change from base case in 1989 (10^6 lb/yr)
Textiles (cont.)	Woven fabric:			
	• Base case	39.5	15.2	-
	• Advanced aqueous	--	6.5	- 8.7
Pulp and paper	Chemical pulp:			
	• Base case: Kraft pulp	90	97	-
	• Alkaline-oxygen pulping	--	71	- 26
	• Rapson effluent free pulping	--	55	- 42
	Newsprint pulp:			
	• Base case: Refinery mechanical pulping	41	17.9	-
	• Thermo-mechanical pulping	--	19.4	+ 1.5
	• Deinking of old newsprint for newsprint manufacture	--	5.6	- 12.3
Chloro-alkali	Base case: Graphite-anode diaphragm cell	313	339	-
	• Dimensionally stable anodes	--	323	- 16

(continued)

TABLE 2. (continued)

Commodity	Process	NO_x emissions in 1974 from base case process (10^6 lb/yr)	Incremental NO_x emissions 1989-1974 (10^6 lb/yr)	Change from base case in 1989 (10^6 lb/yr)
Chloro-alkali (cont.)	• Expandable DSA	--	293	- 46
	• Polymer modified asbestos	--	297	- 42
	• Polymer membrane	--	297	- 42
	• Ion exchange membrane	--	283	- 56
	• Mercury cell	--	351	+ 12

[a]Calculation based on change from base case.

[b]No change from base case process.

Thus, for each process incremental NO_x emissions (1989-1974) are calculated by multiplying the emission factor (lb NO_x/ton of product) by the estimated increase in product production between 1974 and 1989. Total actual emissions from each process in the year 1989 would be the sum of 1974 emissions from the base case process, assuming no retirement at existing facilities, and actual incremental emissions (lb NO_x/year) from the base case and new processes installed between 1974 and 1989.

The estimated increase or decrease in emissions from the alternative processes in relation to the base case process is also shown in Table 2 for the year 1989. This number shows the potential for emission reduction in 1989 using new process technology. It is seen that the greatest potential for emission reduction by new processes exists in the nitric acid industry, followed by the aluminum and cement industries.

All of the process alternatives studied (Volumes III-XV) were aimed at reduction in energy consumption or conversion to less scarce fuel forms. Since fuel consumption usually is directly related to NO_x emissions, these energy-conserving process changes will result in reduction in NO_x emissions. Also, processes aimed at changing the form value of fuel from natural gas or oil to coal were studied. These process changes will generally result in increased NO_x emissions. In alumina production, NO_x emissions may increase if the hydrochloric acid ion exchange method is used, and in the petroleum refining industry, if asphalt combusion is incorporated.

Although the estimated change in emissions shown in Table 2 was based on incremental capacity from 1974 to 1989 only, in some cases as alternative process may be retrofitted on the existing process. For example, NO_x control may be achieved by installing control systems in existing nitric plants or by use of refractory hard metal cathodes installed in existing Hall-Heroult cells in the aluminum industry. The application of new processes as present-day facilities are retired will further increase or decrease the potential effect on the NO_x emissions shown in Table 2.

To give some perspective to the magnitude of NO_x emissions, Table 3 shows the industrial processes category to be a relatively small emitter of NO_x after electric utilities, other stationary fuel combustion sources, and transportation.

Should U.S. industry expand using current (base case) technology, Table 4 shows that estimated controlled NO_x emissions in 1989 would increase by 3.0×10^9 lb compared to NO_x emissions of 1.4×10^9 lb from industrial processes and 13.8×10^9 lb from electric utilities in 1974 (Table 3). However, if all U.S. industry expanded by implementing the technologies considered here that emitted the largest amounts of NO_x, Table 4 shows that the increase in NO_x emissions in 1989 would be 3.7×10^9 lb, or some 23% higher than using conventional technology. On the other hand, if industry expanded by implementing the least NO_x-emitting technology,

TABLE 3. NO_x NATIONWIDE EMISSION ESTIMATES (1974)

Emission source	10^6 lb/yr	% of total
Stationary fuel combustion		
- Electric utilities	13,800	27.6
- Other	12,800	25.6
Industrial processes	1,400	2.8
Transportation	21,200	42.4
Solid Waste	400	0.8
Miscellaneous	400	0.8
TOTAL	50,000	100.0

Source: National Air Quality and Emissions Trend Report, 1975, EPA, Research Triangle Park, N.C.; NTIS PB-263-922.

TABLE 4. ESTIMATED INCREASE IN CONTROLLED NO_x EMISSION 1989-1974 ASSUMING INDUSTRY EXPANDS USING PROCESS TYPES INDICATED (10^6 lb NO_x/yr)

Commodity (vol no)*	Base case process	Using process with largest potential NO_x emissions	Using process with smallest potential NO_x emissions
Steel (III)	108	336	97[b]
Petroleum[a] (IV)	311	373	311
Kraft pulp (V)	97	97	55
Newsprint pulp (V)	18	19	6
Olefins (VI)	389	389	358
Ammonia (VII)	127	344	127
Alumina (VIII)	102	267	90
Aluminum (VIII)	879	879	664
Textiles-knit (IX)	< 1	< 1	< 1
Textiles-woven (IX)	15	15	7
Cement (X)	104	104	18
Flat glass (XI)	106	148	85
Chlorine, NaOH (XII)	339	351	283
Phosphoric acid (XIII)	30	30	3
Copper (XIV)	13	34	5
Fertilizers (HNO_3) (XV)	343	343	< 1
TOTAL	2,982	3,730	2,111

*Volume number of industry report

[a]Assumes East Coast Refinery model applied nationally

[b]Includes credit of 11×10^6 lb NO_x attributed to energy saved in dry quenching and BOP off gas collection.

[c]Credit for steam raised: see discussion on fertilizers in Section 3.

NO_x emissions in 1989 are calculated to increase by 2.1×10^9 lb or some 30% less than by conventional technology. If the national production growth rate projections shown in Table 1 are accurate, then calculated emissions will probably lie somewhere between these extremes, with energy (Btu) saving processes with lower NO_x emissions somewhat balancing the switch from natural and fuel oil to coal. Thus, incentives for the implementation of energy conserving technology can have a significant effect on future NO_x emissions in the industrial sector.

Table 5 shows our estimate of the types of processes likely to be installed in the time period up to 1989 with related NO_x emissions from new plants calculated for the year 1989 assuming no retirement of exisiting facilities. For example, a reading of the industry reports shows that in the copper sector, incremental copper smelting capacity will be effected by one of the newer oxygen or flash smelting processes (e.g., Outokumpu, Noranda, Mitsubishi). If such capacity is installed, anticipated annual NO_x emissions in 1989 would be 5.0 to 9.0×10^9 lb NO_x/yr (Table 5) compared to the 13×10^9 lb NO_x/yr if conventional reverberatory furnace technology were employed (Table 4). Similar judgments were made in other sectors to arrive at total calculated annual emissions of 2.0 to 2.8×10^9 lb NO_x emitted in 1989 from new plant capacity installed in the period 1974-1989.

Examination of the last column in Table 2 shows that greatest reduction compared to the base case processes in lb of NO_x emissions per year can be achieved by selective implementation of new processes in:

- nitric acid manufacture NO_x control
- copper (oxygen or flash processes)
- aluminum (Alcoa chloride, refractory hard metal cathodes)

Process changes in some of the industries shown in Table 2 may be implemented because of feed stock shortages (e.g., manufacture of olefins from low-sulfur naphtha rather than higher sulfur gas oil), and fuel switching (e.g., use of coal in cement making). In other cases, processes may be developed for other reasons, such as development of a domestic alumina industry based on indigenous kaolin clays. Many such processes, based on using coal to the extent possible, would result in significantly higher NO_x emissions, such as ammonia manufacture based on coal. Although the estimated change in emissions listed in Table 2 was based on incremental capacity from 1974 to 1989 only, in some cases an alternative process, or a process modification, may replace existing capacity. For example, in the aluminum industry, refractory hard metal cathodes may be installed in existing Hall-Heroult cells. The application of alternative processes to existing plant capacity will increase the potential effect on NO_x emissions, compared to the estimated effect shown in Table 2. Further perspectives in each of these industry sectors with descriptions of the processes can be obtained from the individual industry sector reports (Volumes III through XV).

TABLE 5. ESTIMATED RANGE IN CONTROLLED NO_x EMISSSIONS IN 1989 FOR NEW PROCESSES LIKELY TO BE IMPLEMENTED

Commodity (vol no)*	Likely types of processes to be implemented in new plants	Calculated range in annual NO_x emissions for new plant capacity-1989 (10^6 lb/yr)
Steel (III)	Coke oven, blast furnace, BOP[c,d]	97-108
Petroleum (IV)	Various refinery options	311-373
Kraft pulp (V)	Kraft, Rapson, alkaline-oxygen	55-97
Newsprint pulp (V)	RMP, TMP, de-inking	6-18
Olefins (VI)	Naphtha, gas oil	358-369
Ammonia (VII)	Heavy fuel oil, coal	155-344
Alumina[a] (VIII)	Bayer, leaching domestic clays	90-267
Aluminum[a] (VIII)	Hall-Heroult, aluminum chloride[a]	592-680
Textiles, knit (IX)	Advanced aqueous, solvent	< 1
Textiles, woven (IX)	Advanced aqueous	6-6
Cement (X)	Preheaters, coal firing	18-104
Flat glass (XI)	Regenerative preheaters, electric furnaces	85-93
Chlor-alkali (XII)	Dimensionally stable anodes, new membranes	283-323
Phosphoric acid: detergent grade (XIII)	Wet acid cleanup	3-3
Copper (XIV)	Oxygen or flash processes[b]	5-9
Fertilizers-nitric acid (XV)	Various NO_x control technologies	1-27
TOTAL		2066-2822

*Volume Number of Industry Report

[a]A significant fraction of the incremental U.S. demand is expected to be imported.

[b]In addition, electric furnaces are expected to be installed based at least partially on scrap.

(continued)

TABLE 5. (continued)

[c]With collection of CO from BOF's.

[d]Base case Gulf Coast Refinery model applied nationally.

IDENTIFICATION OF CROSS-INDUSTRY TECHNOLOGY

Within the industry sectors investigated in this study, the following are the generic findings.

- All things being equal, NO_x emissions can be expected to decrease from many processes for a variety of reasons including:

  Decreased fuel consumption in the process and the power boiler;

  Operation of processes involving combustion at uniform and lower temperatures requiring less excess air; and

  Fuel firing with oxygen in place of air which leads to elimination of the nitrogen coming from the air. (For details see report on copper industry, Volume XIV.)

- On the other hand, NO_x emissions may increase in several process industries for a variety of reasons including:

  Fuel switching from gas to oil to coal. (Coal contains some fixed nitrogen and generally requires a greater amount of excess air. Both factors will normally lead to higher NO_x emissions. For tangentially fired boilers, emission factors calculated from data in AP-42[1] are 0.29 lb/10^6 Btu, 0.33 lb/10^6 Btu and 0.75 lb/10^6 Btu based on gas, oil, and coal burning, respectively.);

  Fuel firing with air preheating which leads to higher flame temperature and greater NO_x emissions; and

  Fuel firing with oxygen-enriched air which generally leads to higher flame temperature and greater NO_x emissions.

R&D AREAS

With regard to NO_x emissions from the new technologies investigated, the following potential areas for R&D have been identified as being worthy of attention by industry, government agencies, or other institutions:

NO_x-Related

- Develop better quantitative data on concentration and gas flow rates from high-temperature operations involving combustion, focusing on sources such as kilns, heaters, etc.

At present, very little information is available on sources other than power boilers, and even there the bulk of the information is for utility boilers.

- Promote NO_x emission reduction at the power boiler by process modifications, by switching to low-nitrogen feedstocks, or by add-on controls. Of particular interest would be fluidized bed combustion.

- Develop better definition of the environmental, health, and ecological impacts of NO_x emissions with respect to obtaining more quantitative knowledge for establishing appropriate emission regulations.

- Promote process alternatives aimed at reduction in energy (Btu) requirements. Energy consumption is related to NO_x emissions and therefore reduction in energy consumption will result in lower NO_x emissions.

Process-Related

Aluminum--

- Consider materials research in the field of producing titanium diboride cathodes suitable in quality to permit long operating life in the Hall-Heroult cell. This development would effect energy savings in the existing aluminum plants, thus reducing NO_x emissions.

Fertilizers--

- For nitric acid plants, it would be beneficial in terms of energy conservation to use processes other than catalytic reduction for NO_x control. Fortunately, such other pcoesses require less capital and lower operating costs. Thus, the industry will likely opt for such alternatives of free choice and will not require outside influence. However, in the process examined, control appears adequate at steady state, but not adequate during start-up and shutdown. Also, the NO_x pollution control devices are complex and may have to be shut down, even though the basic plant continues to operate. Methods of alleviating these problems are worthy of further study. Moreover, it would be useful to study the applicability of these new processes to control NO_x emissions from sources other than nitric acid plants.

Cement--

- Develop and implement a program to sample and analyze NO_x emissions from the fluidized bed which are lower compared to those from conventional long cement kilns. It will be useful to have more data, particularly as a function of operating conditions.

Moreover, it will be beneficial to study the applicability of the fluidized bed in place of kilns in other industries and in the place of power boilers.

Petroleum--

- Develop and implement a test program to characterize NO_x emissions from asphalt combustion. Combustion in both process heaters and in steam generators is important.

SECTION 3

PROCESSES AND POTENTIAL NITROGEN OXIDE EMISSIONS

BASES OF CALCULATIONS

In Volume II (page 19) where the methodology used in this study is described, we indicated that selected State air emission regulations, along with the Federal Government's stationary source performance standards and effluent limitation guidelines, were surveyed to:

- Establish the most probably limits of air and water emissions, and
- Obtain a perspective of the types of pollution control systems to be considered.

In this Section, NO_x control methods and emissions from the process industries (Volumes III to XV) are reviewed. There are two general sources of emissions: the processes themselves and power boilers. While emissions from the power boiler* generally were not considered in the original study, they are included in the present analysis to show the net change in emissions resulting from a process change. Power boilers are assumed to burn coal and their NO_x emissions are estimated at 18 lb/ton of coal burned or 0.75 lb/10^6 Btu (12,000 Btu/lb of coal) or 7.875×10^{-3} lb/kWh (based on the conversion factor of 10,500 Btu/kWh). The New Source Performance Standard (NSPS) limits emissions to 0.7 lb of NO_x/10^6 Btu and may be further lowered to 0.6 lb of NO_x/10^6 Btu. The NO_x emissions from the base case process and process alternatives are described and are summarized for each industry. The NO_x emission factors are estimated, and the effect of these factors on the incremental production from 1974 to 1989 is calculated.

NO_x CONTROL METHODS

Two approaches are available for NO_x control: process modifications, including change to feed containing low nitrogen, and add-on controls, which are further discussed below.

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*Power boilers are used for generation of steam and electricity. Both on-site power boilers and utility power boilers are included.

Process Modifications

Process modifications, generally limited to combustion processes, include reducing flame temperature, starving the fuel for oxygen, or both. Typical techniques for power boilers, which account for almost 50% of the NO_x emissions from stationary sources, include staged combustion, flue gas recirculation, reduced air preheat, steam or water injection, and low excess air firing. With these techniques, reduction in NO_x emissions typically range from 20 to 60% (Table 6). While NO_x emissions are reduced, operating problems generated in these systems include:

- Increased CO concentrations in flue gas,
- Lower boiler efficiency, and
- Increased corrosion in the boiler.

A further process modification which reduces NO_x emissions is the use of fluidized beds. Combustion in fluidized beds occurs at more uniform temperatures which are well below the peak temperatures found in conventional boilers and occurs at low excess air. Both factors result in lower NO_x concentrations. At present, fluidized beds have not been developed for power boiler applications but are increasingly used in the process industries.

TABLE 6. HOW CURRENT NO_x CONTROL METHODS FARE WITH FOSSIL FUELS

Method	NO_x Reduction		
	Gas	Oil	Coal
	(%)	(%)	(%)
Flue Gas Recirculation	60	20	Not Effective
Reduced Combustion-Air Preheat	50	40	Not Competitive
Steam or Water Injection	60	40	Not Competitive
Staged Combustion	55	40	40
Low Excess Air	20	20	20
Reduced Heat-Release Rate	20	20	20
Combined Staging, Low Excess Air and Reduced Heat Release	50	35	40
Change to Fuel with Low % N	Not Effective	40	20

Source: Assessment Overview Matrix, Monsanto Research Corp., EPA Contract 68-02-1874, September 1976.

A detailed description of the use of the fluidized bed in the cement industry (in place of the long dry kiln) is given in Volume X, page 40.

Add-On Technology

In the United States, add-on NO_x control technology is in the development stage, except for application to sources such as nitric acid plants. Thus except for nitric acid plants, NO_x emissions in this report are estimated on the basis of no add-on technology. NO_x concentrations in the untreated tail gas from a nitric acid plant are in the range of 3,000 ppm compared to a 100-600 ppm concentration in the flue gas from combustion processes. NO_x control methods for nitric acid plants are described in detail in Volume XV, page 24.

PETROLEUM REFINING INDUSTRY

Base Case Process - 1985 Refinery

A description of the petroleum refining industry is presented in Volume IV, page 9. In assessing the impact of process changes in the refining industry, a 1985 refinery configuration was used as a baseline. The reasons for using this approach are given in Volume IV, page 22. Three configurations were selected to represent the local conditions: East Coast, Gulf Coast, and West Coast. Among the process options analyzed, two affect NO_x emissions from the refineries. These are:

- use of asphalt in process heaters (evaluated within the context of the East Coast refinery cluster model); and
- use of asphalt to generate on-site electricity and process steam (evaluated within the context of the Gulf Coast refinery cluster model).

Further details are presented below.

East Coast Refinery

Base Case Process--

The base case East Coast refinery is described in Volume IV, page 23. The energy intake in this refinery (in terms of crude oil, fuel, steam and electricity) is 1.31×10^{12} Btu/day and production is equivalent to 1.19×10^{12} Btu/day (Volume IV, page 35).

The major airborne pollutants emitted by refineries have been previously identified in Volume IV, page 22. The emission factors summarized in AP 42[1] were used to determine NO_x emissions from the base case refinery. The NO_x emissions are: 10,129 lb of NO_x/day from gas-fired heaters and boilers; 27,956 lb of NO_x/day from oil-fired heaters and boilers; and 4,416 lb of NO_x/day from fluid catalytic crackers. The total emissions of 42,501 lb of NO_x/day are equivalent to an emission factor of 35.84 lb

of $NO_x/10^9$ Btu of refinery output. These emissions are not controlled and no add-on control technology is available at this time.

Estimated emissions from the power boiler (off-site utility boiler) are 6,675 lb of NO_x/day, equivalent to 5.63 lb of $NO_x/10^9$ Btu of refinery output.

Process Option 1 - Direct Combustion of Asphalt in Process Heaters and Boilers--

A detailed description for this alternative appears in Volume IV, page 32. Utilizing asphalt for combustion is intended primarily to upgrade the overall thermal efficiency within the refinery. Part of the refinery gas (36.6%) and all of the fuel oil is displaced by asphalt. The energy balances for the base case process and the alternative are summarized in Volume IV, page 35. In the alternative process NO_x emissions are increased due to the higher nitrogen content of the asphalt. However, the NO_x emission factor for asphalt combustion is assumed to be equal to the emission factor for oil combustion due to lack of data. The estimated NO_x emissions based on this assumption from the asphalt combustion, as shown in Volume IV, page 38, are 1,729 lb/hour, or 41,496 lb/day. Emissions from the gas burned in the process heaters will be equal to 6,422 lb of NO_x/day. The emissions from the catalytic crackers (4,416 lb of NO_x/day) are not affected by the process change. The total emissions, 52,334 lb of NO_x/day, are equivalent to 44.13 lb of $NO_x/10^9$ Btu of refinery output.

Electricity consumption in the alternative process is the same as in the base case process and therefore the power boiler emissions are the same, 5.63 lb of $NO_x/10^9$ Btu of refinery output.

Gulf Coast Refinery

Base Case Process--

The base case refinery configuration in the year 1985 located at the Gulf Coast is described in Volume IV, page 23. Total energy input in the base case refinery is $1,358 \times 10^9$ Btu/day and production is equivalent to $1,197 \times 10^9$ Btu/day.

NO_x emissions from this base case process were developed in a similar way as those for the East Coast base case refinery.

The emissions include 40,999 lb of NO_x/day from heaters and boilers and 5,694 lb of NO_x/day from fluid catalytic crackers. The total emissions of 46,693 lb of NO_x/day are equivalent to 39.01 lb of $NO_x/10^9$ Btu of refinery output.

Based on electricity consumption equivalent to 9.2×10^9 Btu/day (Volume IV, page 70) the estimated emissions from the power boiler are 5.76 lb of $NO_x/10^9$ Btu of refinery output.

Process Option 1 - On-Site Electric Power Generation by Combustion of Asphalt--

In this process alternative, electric power is generated within the refinery rather than purchased from a local electric utility. The fuel is assumed to be asphalt. A simplified flow sheet for this alternative shown in Volume IV, page 69.

Generation of electric power within the refinery neither conserves assuming that the internal and external power plants would operate at the same efficiencies. In effect, the form value of the asphalt is upgraded to a higher form value of electric power for refinery use. The design capacity of the generator, as shown in Volume IV, page 77, is 36.5 megawatts.

This process alternative will result in increased on-site NO_x emissions. NO_x emissions from the power boiler are 4,234 lb/day (Volume IV, page 73), equivalent to 3.56 lb of $NO_x/10^9$ Btu of refinery products. NO_x emissions from the process are not affected (39.01 lb of $NO_x/10^9$ Btu of refinery products).

Summary

NO_x emissions from the base case processes and the alternatives are summarized in Table 7. There are no significant changes in the emissions. In the direct combustion of asphalt in process heaters and boilers, the emissions are increased by 20% as compared to the base case process. The emissions in the alternative processes are based on the assumption that the emission factor for asphalt combustion is equal to the emission factor for oil combustion.

CEMENT INDUSTRY

Base Case Process - Long Dry Rotary Kiln

The base case process selected for the cement industry was the long dry rotary kiln. Hydraulic cement is a powder made by burning lime, silica, alumina, iron, and magnesia together in a kiln and then pulverizing the product. The production of finished cement from raw materials involves four steps: crushing, grinding, clinkering, and finish grinding. In the dry process, dry grinding is done. This is very much like wet grinding, except that no water is added and the material is ground dry, usually at 1% moisture content or less. A detailed description of the process is given in Volume X, page 84.

Nitrogen oxides can form at combustion temperatures during clinkering in the kiln (2,600-3,000°F). The emission factor for NO_x reported in AP-42[1] is 2.6 lb/ton of cement produced. A kiln producing 80 tons of cement clinker/hour will produce about 240,000 lb of outlet gas/hour, or about 92,000 acfm. Based on this, the NO_x concentration in the exit gas will be about 150 ppm. NO_x emissions from cement kilns are not

TABLE 7. ESTIMATED NO_x EMISSIONS - PETROLEUM REFINERY INDUSTRY
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	Estimated emission factor ($lb/10^9$ Btu of refinery output) Process	Power boiler	Total	Change from base case	NO_x emissions[a] (10^6 lb/yr) 1974**	1989-1974*
Base case: East Coast refinery	35.84	5.63	41.47	0	1,244	311
• Direct combustion of asphalt in process heaters and boilers	44.13	5.63	49.76	+ 8.29	-	373
• Flexicoking	35.84†	5.63	41.47†	0	-	311†
Base case: Gulf Coast refinery	39.01	5.76	44.77	0	1,343	336
• Onsite electric power by combustion of vacuum bottoms	39.01	3.56	42.57	- 2.2		319
Base case: West Coast refinery	(a)	(a)	(a)	(a)		
• Hydrocracking of heavy bottoms	(a)	(a)	(a)	(a)		
• High purity hydrogen production via partial oxidation of asphalt	(a)	(a)	(a)	(a)		

*Based on increment in production from 1974-1989 = 7.5 quads.

(continued)

TABLE 7. (continued)

** Estimated 1974 emissions, based on the total emission factor of 41.47 lb of NO_x/10^9 Btu of refinery output are 41.47 x 30 x 10^6 = 1,244 x 10^6 lb and based on the emission factor of 44.77 lb of NO_x/10^9 Btu of refinery output are 44.77 x 30 x 10^6 = 1,343 x 10^6 lb for East Coast and Gulf Coast models, respectively.

† Calculation assumes same emissions as base case: East Coast refinery model

[a] No change from base case

controlled and no add-on control technology is available. The emissions from the power boiler are estimated at 1.2 lb of NO_x/ton of cement.

Process Option 1 - Suspension Preheater Process Alternative--

The suspension preheater is a modification or addition to the cement rotary kiln. It is attached to the raw feed inlet end of the kiln, totally replacing the preheating zone. The suspension preheater preheats the raw material and also accomplishes a considerable amount of raw material calcination. Suspension preheaters typically heat cold raw feed to approximately 1,400°F and accomplish 30-40% of the total calcination or thermal decomposition of the calcium carbonate, the main component of the raw feed. Consequently, with the suspension preheater, the rotary kiln receives hot and partially calcined raw material. There are several variations on the suspension preheater and these are described in Volume X, page 19.

As reported in Volume X, page 7, the energy consumption with the suspension preheater is lower than that of the base case process, primarily due to a significantly lower fuel energy requirement. About 20-25% energy is saved overall.

The concentration of nitrogen oxide found in the combustion gas from both the long dry rotary kiln and the preheater system will probably be equivalent because fuel is burned in the same way in both systems. However, the quantity of nitrogen oxide generated per ton of cement clinker produced by the suspension preheater kiln will be about 20-25% less than that produced by the long kiln, because of the higher thermal efficiency of the suspension preheater. Thus, the NO_x emissions from the suspension preheater kiln will be about 2.0 lb/ton of cement produced.

The electrical power consumed in the alternative process is also reduced by 15-20% from that of the base case process due to the energy recovery (Volume X, page 30), and therefore the emissions from the power boiler are reduced to an estimated value of 1.0 lb of NO_x/ton of cement.

Process Option 2 - Flash Calciner Process Alternative--

Although the design of flash calcining systems varies, the main feature which characterizes the flash calciner rotary kiln is the flash calcining vessel added between the rotary kiln and the suspension preheater. A detailed process description is given in Volume X, page 34.

The flash calciner arrangement (described in Volume X, page 23) uses a considerable amount of excess combustion air in burning the fuel in the rotary kiln so that enough air is present in the combustion gases leaving the kiln to permit combustion of the fuel in the flash calcining vessel.

The several advantages of slash calciners cited in Volume X, page 36, include reduced nitrogen oxide emissions. Since 50-60% of the total fuel burned in this system is burned in the flash calciner and the temperature of the flash calciner is maintained at only about 1,500 °F, the nitrogen oxides formed in this vessel are reported to be considerably less than those formed in the high-temperature, free-standing flame which is burned in a rotary kiln. Also, the flash calciner operates at a low and uniform temperature and oxygen content. The NO_x emissions are estimated in the range of 50-100 percent of those from the suspension preheater alternative.

The electrical power consumed in the process is comparable to that consumed in the suspension preheater alternative and therefore the estimated emissions from the power boiler are the same -- 1.0 lb of NO_x/ton of cement.

Process Option 3 - Fluidized-Bed Process Alternative--

The only difference between the fluidized-bed, cement-making process and the conventional process occurs in the high-temperature clinkering step. All of the other steps are essentially identical. A detailed description of the process is given in Volume X, page 40. If the energy consumption in the fluidized bed and in the long kiln (Volume X, page 46) is compared, the fuel consumption in the fluidized bed is seen to be about 10% higher. However, there is a net electricity generation in the fluidized bed process.

Combustion conditions in the rotary cement kiln favor NO_x formation due to peak flame temperatures associated with the combustion of fuel in suspension as well as the existence of regions of high oxygen concentration due to the absence of good fuel-air mixing, further enhanced by in-leakage of ambient air to the rotary kiln seal. By contrast, the fluidized-bed reactor operates with both a uniform temperature (constant at 2,400°F) and oxygen distribution which prevents conditions for high NO_x production from occurring.

Volume X, page 58, shows NO_x emissions from a fluidized-bed reactor and a rotary kiln both being operated at 2,400°F to produce solid products. The fuel used during this test was oil and the percent stoichiometric air was the independent variable. The fluidized bed clearly generates significantly lower NO_x emissions than the rotary kiln. At high excess air the flue gas from the rotary kiln contains 150 ppm of NO_x and the flue gas from the fluidized bed contains 45 ppm NO_x. The 150 ppm NO_x concentration in the flue gas from the rotary kiln is consistent with the emission factor of 2.6 lb of NO_x/ton of cement produced. The fuel consumed in the fluidized bed is approximately 10% higher. Based on the decreased NO_x concentration in the flue gas and 10% increase in fuel consumption, it can be expected that the NO_x emissions from the fluidized bed will be about one-third those from the rotary kiln. Therefore, the emissions in the flue gas from the fluidized bed will be about 0.7-0.8 lb of NO_x/ton of cement produced.

Since there is a net electricity generation in the fluidized bed process, emissions at the power boiler are reduced by an estimated 0.1 lb of NO_x/ton of cement.

Process Option 4 - Conversion to Coal Fuel from Oil and Natural Gas Process Alternative--

The process description using coal as a fuel in the cement kiln is described in Volume X, page 60. NO_x emissions from coal combustion cannot be estimated in this process but are expected to be higher than those in the base case process.

NO_x emissions from the power boiler are not affected by switching the fuel from oil or gas to coal in the cement kiln.

Summary

NO_x emissions from the base case process and the alternatives are summarized in Table 8. The emissions are uncontrolled, and no add-on control technology is available. Emissions from the base case process and from the conversion to coal from natural gas and oil alternative are essentially the same and are somewhat lower than those from the suspension preheater and flash calciner alternatives. The emissions are significantly reduced in the fluid bed alternative due to reduced emissions from both the process and the power boiler. The process emissions are reduced due to the uniform temperature distribution in the fluid bed.

OLEFINS INDUSTRY

Ethylene Production

Base Case Process - Ethylene Production Based on Ethane and Propane Cracking--

The base case technology selected for the assessment of the domestic olefin industry was ethane and propane (E-P) cracking. A detailed description of the process of producing ethylene from ethane and propane is given in Volume VI, page 17.

There are no NO_x emissions as such from the process. However, some NO_x emissions are expected from the fuel used in heaters, steam generators, and power boilers. Natural gas is used as a fuel in the heaters and steam generators. The NO_x emission factor in the olefin industry can be estimated based on the fuel and electricity consumption (Volume VI, page 28). As shown in Table 9, the emission factor is estimated at 12.45 lb of NO_x/ton of ethylene produced. Emissions from the power boiler are estimated to be 1.35 lb of NO_x/ton of ethylene.

Process Option 1 - Ethylene from the Pyrolysis of Naphtha Alternative--

Pyrolysis of naphtha already accounts for 7% of domestic ethylene production and is the predominant technology used in Europe and Japan. This process alternative is described in Volume VI, page 22.

TABLE 8. ESTIMATED NO_x EMISSIONS - CEMENT PRODUCTION
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	Estimated emission factor (lb of NO_x/ton cement) Process	Boiler	Total	Change from base case	NO_x emissions[a] (10^6 lb/yr) 1974**	1989-1974*
Base case: Long dry kiln	2.6	1.2	3.8	0	300	104
• Suspension preheater	∿ 2.0	1.0	3.0	-0.8	--	82
• Flash calciner	< 2.0	1.0	< 3.0	-0.8	--	82
• Fluidized bed	∿ 0.7-0.8	(-0.1)	∿ 0.65	-3.15	--	18
• Coal as fuel instead of gas or oil in long dry kiln	2.6	1.2	3.8	0	--	104

* Based on the incremental production of cement from 1974 to 1989; 27.3×10^6 tons.

** The NO_x emissions based on the emission factor of 3.8 lb/ton of cement in the year 1974 are $3.8 \times 79 \times 10^6 = 300 \times 10^6$ lb.

TABLE 9. NO_x EMISSION FACTORS - OLEFINS INDUSTRY
BASES: 1 TON OF ETHYLENE AND NO ADD-ON
TECHNOLOGY FOR NO_x CONTROL

	Ethylene production		
	Ethane propane cracking	Naphtha pyrolysis	Gas-oil pyrolysis
Process heaters:			
Natural gas, 10^6 Btu*	15.6	20.6	29.4
Combustion emissions lb/10^6 ft^3	120	120	120
NO_x emissions, lb/ton ethylene	1.78	2.35	3.36
Steam regenerators:			
Natural gas, 10^6 Btu*	16.0	0	0
Combustion emissions lb/10^6 ft^3	700		
Oil, 10^6 Btu	0	12.4	11.0
Combustion emissions* lb/10^3 gal		105	105
NO_x emissions, lb/ton ethylene	10.67	8.68	7.7
NO_x emission factor, lb/ton ethylene	12.4	11.0	11.1
Boiler emissions:			
Electric power, 10^6 Btu	1.8	2.2	3.0
NO_x emissions, lb/ton ethylene	1.35	1.65	2.0
Total NO_x emissions, lb/ton of ethylene	13.8	12.7	13.1

*Compilation of Air Pollution Emission Factors, Second Edition, AP-42, published by USEPA, March 1975.

Source: Arthur D. Little, Inc., estimates.

As in the base case process, NO_x is not present in the process emissions but occurs in heaters, steam generators, and power boilers. The emission factor is estimated at about 11.0 lb of NO_x/ton of ethylene produced (Table 9). The emissions from the power boiler are estimated to be 1.65 lb of NO_x/ton of ethylene.

Process Option 2 - Ethylene from the Pyrolysis of Gas-Oil Alternative--

Several plants now being constructed will use gas-oil as feed. The design of such plants is well established at the commercial level and the practice is clearly going to become common as ethylene producers move to assure themselves of some flexibility in their choice of feedstock. A process description for ethylene production based on gas-oil is given in Volume VI, page 27.

As in the above two methods for the production of ethylene, NO_x emissions are not generated by the process. However, NO_x emissions will be present in the gases from the heaters, steam generators, and power boilers. The estimated emission factor (Table 9) is about 11.1 lb of NO_x/ton of ethylene. The emissions from the power boiler are estimated to be 2.0 lb of NO_x/ton of ethylene.

Gas-Oil Cracking

Base Case Process - Vacuum Gas-Oil Cracking with Conventional Technology--

The base case process, vacuum gas-oil cracking with conventional technology, is described in Volume VI, page 109. There are no NO_x emissions from this process. Emissions from the power boiler cannot be estimated because energy consumption data are not available.

Process Option 1 - Fluid Bed Cracking of Petroleum Residues (AIST)--

This process employs a twin fluidized-bed reactor system. The thermal cracking of heavy oils is accomplished in a fluidized bed of coke particles. After providing the heat for cracking, the coke is transferred to the regenerator where a portion of it is burned with air to reheat the fluidized bed before being returned to the reaction vessel. The cracking reactor operates at 1,290-1,560°F and the coke regenerator at 1,470-1,700°F. Both units are operated under atmospheric pressure conditions. A description of the process is given in Volume VI, page 119.

Since air is used in this process there is an excellent probability that NO_x formation will occur. The temperature distribution in the regenerator should be highly uniform which is typical of a fluidized state. In the cement industry, NO_x emissions in the flue gas from the fluidized-bed reactor operated at 2,400°F and at high excess air are 45 ppm (Volume X, page 58). The coke regenerator is operated only at 1,470-1,700°F. Therefore, NO_x concentration in the regenerator flue gas is expected to be much lower than 45 ppm.

TABLE 10. ESTIMATED NO_x EMISSIONS - OLEFINS INDUSTRY
BASES: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	Estimated emission factor (lb NO_x/ton ethylene) Process	Power boiler	Total	Change from base case	NO_x emissions* (10^6 lb/yr) 1974**	1989-1974*
Base case:						
E-P process	12.4	1.4	13.8	0	169	389
• Naphtha process	11.0	1.7	12.7	- 1.1	--	358
• Gas-oil process	11.1	2.0	13.1	- 0.7	--	369

* Based on increment in production from 1974-1989 - 28.2 million tons.

** Estimated 1974 emissions, based on the total emission factor of 13.8 lb of NO_x/ton of ethylene, are 13.0 x 13 x 10^6 lbs.

Summary

The NO_x emissions for theylene production are summarized in Table 10. Emissions from the base case process and alternative processes are comparable. The emissions are not controlled and no add-on control technology is currently available.

ALUMINA AND ALUMI''UM INDUSTRY

Alumina Production

Base Case Process - Bayer Process for Producing Alumina--

The Bayer process for producing alumina is based on imported bauxite. The process includes: digestion of ground bauxite, removal of impurities, precipitation of aluminum trihydrate, treatment of spent liquor to regenerate the caustic, and calcination of aluminum trihydrate to produce pot feed alumina. A detailed description of the process is given in Volume VIII, page 106.

NO_x emissions may result from calcination of limestone and of aluminum trIdydrate. NO_x concentrations in the flue gas may be comparable to the concentrations in the flue gas from the long dry (rotary) kiln (150 ppm) in the cement industry (Volume X, page 58). The flue gas flow rate is in the proportion to the rate at which fuel is consumed in a kiln. The fuel consumed in the long dry cement kiln is equivalent to about 4.6×10^6 Btu/ton (Volume X, page 30) and estimated emissions are 2.6 lb of NO_x/ton of cement. The fuel consumed in lime calcination ($0.21\text{-}0.43 \times 10^6$ Btu/ton of alumina) and alumina calcination ($2.8\text{-}3.0 \times 10^6$ Btu/ton of alumina) is about 4.3×10^6 Btu/ton of alumina (Volume VIII, page 111). Therefore, the estimated emissions from the kilns are 2.43 lb of NO_x/ton of alumina.

Fuel consumed in the steam generators associated with the Bayer process is equivalent to $4.4\text{-}11.3 \times 10^6$ Btu/ton of alumina (Volume VIII, page 111). The expected emissions based on natural gas as fuel (average consumption of 7.3×10^6 Btu/ton of alumina) are then 4.87 lb of NO_x/ton of alumina (based on 275 kWh/ton of alumina, as reported in Volume VIII, page 19).

Process Option 1 - Hydrochloric Acid Ion Exchange Process Alternative--

This process includes dehydration of the raw clay, leaching with hydrochloric acid, separation of residue, purification of the solution by amine ion exchange, crystallization of aluminum chloride, decomposition and calcination to obtain alumina. A detailed description of the process is given in Volume VIII, page 22. No commercial plant embodying this process has ever been built (Volume VIII, page 27) and therefore the estimated emissions represent crude numbers.

NO_x emissions would result from the combustion of fuel in the kilns, steam generators, and power boiler. The total natural gas consumed by the process (excluding the power boiler) is equivalent to 37.8×10^6 Btu/ton of alumina (Volume VIII, page 31). A breakdown of fuel consumption by

operation is not available. Assuming NO_x emissions to be in proportion to the fuel consumed, we estimate the emissions would be equal to 21.4 lb of NO_x/ton of alumina (NO_x emissions are slightly less from steam generators than from the kilns--based on equal fuel consumption--see base case process for comparison). Estimated emissions from the power boiler are 1.06 lb of NO_x/ton of alumina (based on 134 kWh/ton of alumina, as reported in Volume VIII, page 31).

Process Option 2 - Nitric Acid Ion Exchange Process Alternative--

This process includes: calcining the kaolin clay, leaching the calcined clay with hot nitric acid, separating the clay-insolubles, removing the iron and other impurities, recovering the alumina by hydrolysis, recovering the nitric acid, and calcining to obtain alumina.

In this process, coal and oil are used as fuel. NO_x is present in several waste gas streams (Volume VIII, page 38) and in the flue gas from the combustion processes. Again, assuming that NO_x emissions are in proportion to the 25.3×10^6 Btu of fuel used (Volume VIII, page 40) estimated emissions would be 14.3 lb NO_x/ton alumina. It should be recognized that it has been claimed that NO_x emissions may be reduced somewhat by alkali scrubbing; used for SO_x removal (since coal is assumed to be the fuel in this option).

Emissions from the power boiler are estimated to be 1.1 lb of NO_x/ton of alumina, based on consumption of electrical power equal to 139 kWh/ton of alumina (Volume VIII, page 40).

Process Option 3 - Toth Alumina Process Alternative--

This process involves the chlorination of alumina-containing raw materials in the presence of carbon to produce aluminum chloride vapor and other volatile chlorides. These products are subsequently purified to eliminate other metal chlorides and then oxidized to alumina and chlorine for recycle. The details of the process are given in Volume VIII, page 39.

Gaseous emissions from the process which may include NO_x are off-gases from the dehydration step and from feed and product calcination. There is no existing plant or large pilot plant (Volume VIII, page 43), and therefore emission data are not available. The total fuel consumed in the process is equivalent to 9.09×10^6 Btu/ton of alumina. Assuming an NO_x formation rate in proportion to the fuel consumed (comparing with the base case process), we estimate the emission rate would be 5.72 lb of NO_x/ton of alumina. Estimated emissions from the power boiler are 2.62 lb of NO_x/ton alumina, based on electrical consumption of 333 kWh/ton of alumina (Volume VIII, page 50).

Aluminum Production

Base Case Process - Hall-Heroult Process--

This process involves reduction of alumina to aluminum using electrolytic cells. Many existing plants use Soderberg electrodes while new plants are expected to use prebaked electrodes which consume less energy. A detailed description of the process is given in Volume VIII, page 52.

The major NO_x emissions from this process are from the power boiler and are estimated at 123 lb of NO_x/ton of aluminum, based on the consumption of electrical energy in existing plants (Volume VIII, page 116). The newer plants consume less electrical energy (12,000 kWh/ton of aluminum for the newer plants versus 15,600 kWh/ton of aluminum for older plants) and therefore the emissions from the power boiler are reduced to an estimated value of 94.5 lb of NO_x/ton of aluminum. The process emissions from fuel combustion are difficult to estimate from the information presented in Volume VIII (Appendix B) but are expected to be small at the expected flame temperatures of 2000°F to 2400°F. For example, for a copper reverberatory furnace operating in this temperature range we estimate about 8 lb of NO_x/ton of copper (see "Copper Industry" in this report) requiring 19 to 24 million Btu of fuel (Volume XIV, page 37). This amounts to about 0.4 lb NO_x/million Btu. Assuming NO_x emissions are proportional to fuel used, the estimated 6.6×10^6 million Btu of fuel required in the Hall-Heroult process (Volume VIII, page 115) would result in 2.6 lb NO_x/ton aluminum.

Process Option 1 - Alcoa Chloride Process Alternative--

This process starts with pot feed alumina from the Bayer process. The alumina is converted into aluminum chloride by chlorination in the presence of carbon to form volatile aluminum chloride. This, in turn, is purified and fed to the electrolytic cells to produce molten aluminum.

Energy consumed by the process includes No. 6 fuel oil equivalent to 24.85×10^6 Btu/ton of aluminum (Volume VIII, page 69. Part of the fuel is used in the coking step (fluid bed operated at 1650°F), (Volume VIII, page 57). The expected NO_x emissions from this source are expected to be minor. A breakdown of the fuel consumption is not available and, therefore, NO_x emissions from other sources, such as the dryer and calciner, cannot be estimated. However, because of the relatively low temperature of these operations (1600°C, Volume VIII, page 61) the emissions should be small compared to those from the power boiler. Energy for casting should be comparable to the base case of about 4×10^6 Btu/ton aluminum (Volume VIII, page 115). Assuming emissions to be proportional to fuel used as in the base case above, we calculate 1.6 lb NO_x/ton aluminum for casting. Based on electricity consumption of 1,500 kWh/ton of aluminum (Volume VIII, page 69) we estimate emissions from the power boiler to be 83 lb of NO_x/ton of aluminum.

Process Option 2 - Refractory Hard Metal Cathodes Process Alternatives--

This process is based on Bayer alumina and uses titanium diboride cathodes instead of conventional carbon cathodes. The cathodes are assumed to be retrofitted in existing large cells to increase production and reduce energy consumption (Volume VIII, page 74). A detailed process description is given in Volume VIII, page 68.

NO_x emissions are expected from combustion processes and the power boiler. The fuel consumption is equivalent to 6.1×10^6 Btu/ton of aluminum (Volume VIII, page 76). Assuming as we did for the base case, 0.4 lb $NO_x/10^6$ Btu of fuel, we calculate process emissions to be 2.4 lb of NO_x/ton aluminum. Estimated emissions based on power consumption of 12,480 Btu/ton of aluminum (Volume VIII, page 76) are 98.3 lb of NO_x/ton of aluminum from the power boiler.

Process Option 3 - Combination of the Toth Clay Chlorination Process and the Alcoa Chloride Process Alternative--

The details of the combined process are given in Volume VIII, page 79. This combined process has all of the effluent probelms of the Toth alumina process plus some of the effluent problems of the Alcoa process.

The estimated emissions from the Toth process include 5.72 lb of NO_x/ton of alumina. For aluminum production, 1.93 tons of alumina/ton of aluminum are required (Volume VIII, pages 50 and 81). Therefore, emissions are estimated to be 11.0 lb of NO_x/ton of aluminum.

We estimate the consumption of electrical energy in the combination process to be 10,637 kWh/ton of aluminum (Volume VIII, page 81), resulting in emissions of 83.8 lb of NO_x/ton of aluminum.

Thus, the total emissions from the alternative process are 11.0+83.8= 94.8 lb of NO_x/ton of aluminum. These emissions are lower than the emissions from combined Bayer & Hall process (112.8 lb of NO_x/ton of aluminum for new plants and 141.3 lb of NO_x/ton of aluminum for existing plants).

Summary

The NO_x emissions from the base case processes and alternatives are summarized in Table 11. In the alumina industry, a significant fraction of the emissions result from fuel combustion either in a process or in steam generators, except in the case of the nitric acid leaching process. (The emissions from this process cannot be estimated.) Emissions are considerably increased in the hydrochloric acid leaching process. NO_x emissions from this process are not controlled and no add-on control technology is available.

In the aluminum industry, the process emissions are small compared to those from the power plant. The electrical energy used per ton of aluminum is significantly higher compared to electrical energy consumption

in other industries. NO_x emissions from the power boiler are estimated to range from 80 to 125 lb/ton of aluminum (Table 11). In the alternative processes, the NO_x emissions are reduced by 20 to 30%.

GLASS INDUSTRY

Base Case Process - Regenerative Furnace

The base case process selected was the natural gas-fired furnace with cold charge. A detailed description of the furnace is given in Volume XI, page 17. Operating conditions for the base case process are as follows:

Furnace type: Side port, regenerative
Fuel: Natural gas
Glass type: Soda lime
Plant location: East North Central
Pull rate: 200 tons per day
Feed rate: 240 tons per day
Efficiency: 90%, or 180 tons per day.

The typical glass melting operation is described in detail in Volume XI, page 19. A glass-melting furnace has both particulate and gaseous emissions which must be controlled.

The major gaseous pollutant is nitrogen oxide which is formed during the combustion of natural gas. Because of the high temperatures required in the furnace, the gas combustor must be operated at temperatures favorable to nitrogen oxide formation. The highest temperature in the melter is about 2,920°F. The NO_x emission factor for the glass melting furnace is 8 lb/ton of glass produced, as shown in Volume XI, page 27. The estimated NO_x emissions from the power boiler to generate electricity are 0.15 lb/ton of glass.

The only viable control technique for nitrogen oxide at the present time is maintaining the proper combustion conditions in the furnace. For example, low-excess air firing and no air preheating both produce minimum nitrogen oxide emissions. As is the case with utility boilers, the control of nitrogen oxides is based or modification of combustion conditions.

Process Option 1 - Coal Gassification Alternative--

Coal gasification processes include, in some variation, the following steps: coal handling and storage, coal preparation, gasification, oxidant feed facilities, and gas cleaning. The gas produced from coal gasification is used as a fuel source in the glass furnace. The details of the process are given in Volume XI, page 32.

When coal gasification is used to generate the gaseous fuel for the glass-melting furnace, the major environmental difference is not in the glass-making process, but rather in the fuel-generating process The gas produced in the coal gasifier is expected to contain very little or no NO_x. Most of the nitrogen is in the reduced form as NH_3 and is scrubbed

TABLE 11. ESTIMATED NO_x EMISSIONS - ALUMINA AND ALUMINUM INDUSTRY
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	Estimated emission factor (lb NO_x/ton of product) Process	Power boiler	Total	Change from base case	NO_x emissions* (10^6 lb/yr) 1974**	1989-1974*
Alumina						
Base case: Bayer	7.3	2.17	9.47	0	72.9	102
• Hydrochloric acid ion exchange	21.4	1.06	22.46	+ 12.99	--	267
• Nitric acid ion exchange	14.3	1.09	15.39	5.92	--	108
• Clay chlorination (toth)	5.72	2.62	8.34	- 1.13	--	90
Aluminum						
Base case: Hall-Heroult (current practice)	∿ 2.6	123	125.6	0	628	879
• Hall-Heroult (new)	∿ 2.6	94.5	97.1	- 28.5	--	680
• Alcoa chloride	∿ 1.6	83.0	84.6	- 41.0	--	592
• Refractory hard metal cathode	∿ 2.4	98.3	100.7	- 24.9	--	705
Base case: Bayer and Hall-Heroult†	∿16.7	127.2	143.9	701†	--	1007
• Clay chlorination (toth) and aloca chloride†	11.0	83.8	94.8	- 49.1	--	664

(continued)

TABLE 11. (continued)

* Based on increments in production from 1974 to 1989 -- 10.75 million tons of alumina/year or 7.0 million tons of aluminum/year.

** Estimated 1974 emissions for alumina, based on the emission factor of 9.47 lb of NO_x/ton of alumina, are $9.47 \times 7.7 \times 10^6 = 72.9 \times 10^6$ lb of NO_x from alumina production; for aluminum NO_x emissions based on the emission factor of 125.6 lb of NO_x/ton of aluminum, are $125.6 \times 5 \times 10^6 = 628 \times 10^6$ lb of NO_x from aluminum production. The ratio of Al_2O_3 and Al production, 1.54 is different from 1.93 (reported in Volume VIII, p. 54) because imported alumina is used for production of Al at some plants.

† Bayer Process plus Hall-Heroult (existing) is used for comparative analysis based on 1.93 tons alumina used per ton aluminum.

out in the gas-cleaning system. The only difference between the base case process and the heating of the glass furnace using gas from a coal gasifier is that the exhaust gas from the coal gasifier case will be slightly greater in volume than that of the base case. There is about a 10% difference in the gas flows between the coal gasification case and the base case. As a consequence, the NO_x emissions will be increased by about 10% compared to those from the base case process and will amount to an estimated 8.8 lb NO_x/ton glass. The NO_x emissions from the power boiler are comparable to those from the base case process, about 0.15 lb/ton of glass.

Process Option 2 - Direct Coal-Firing Process Alternative--

In this option, pulverized coal is used directly in burners to supply the energy. The details of the process are given in Volume XI, page 45.

The main difference between the base case process and direct coal firing is that coal is a slightly more difficult fuel to burn and will require a greater amount of excess air to achieve proper combustion. The volumetric gas flow rate of the effluents is expected to be the same as the volumetric flow rate from the coal gasifier system. Thus we estimate that will be more than 8.8 lbs NO_x found in process option 1. However, we believe it should be less than the 11.2 lb NO_x/ton glass found in process option 3. As a result we use an average value of 10 lb NO_x/ton glass for process emissions in this option. The NO_x emissions from the power boiler are comparable to those from the boilers in the base case process, about 0.15 lb/ton of glass.

Process Option 3 - Coal-Fired Hot Gas Generation (COHOGG) Process Alternative--

This system generated a hot gas by separating char and volatiles, burning the char, and then mixing the products of combustion with the volatiles and burning them together. A pneumatic conveying system feeds powdered coal to the pyrolyzer along with limestone or a mixture of limestone and sodium chloride. The outlet temperature of the gases leaving the afterburner is 3,000°F. These hot gases are used in the glass-melting furnace to heat the glass batch. The details of the process are given in Volume XI, page 48.

The gas volume to the glass furnace is higher with the COHOGG process because of the efficiency losses inherent in the system. The operating temperatures in the glass furnaces are the same, and therefore pollution control problems will be the same. The NO_x emissions are expected to increase directly with the gas volume and nitrogen in the coal. The volumetric gas flow from the COHOGG process is estimated to be 40% higher than the volumetric gas flow rate from the base case process. Consequently, estimated NO_x emissions of at least 11.2 lb of NO_x/ton of glass are generated. The NO_x emissions from the power boiler are comparable to those from the base case process, about 0.15 lbs/ton glass.

Process Option 4 - All-Electric Melting Alternative--

Molten glass can be heated by the passage of an electric current. Both the design and the operation of an all-electric, glass-melting furnace differ greatly from those of the typical natural gas-fired, regenerative furnace. The electric furnace without its regenerative checker structure is a much simpler design. The details of the electric furnace are given in Volume XI, page 53.

The option to electrically heat glass-melting furnaces results in a shift in the environmental problems from the furnace to the electric power plant. In this case the only exhaust from the glass-melting furnace is from the decomposition of carbonates, sulfates, nitrates, etc., in the glass batch. The NO_x emissions will be greatly reduced. In the fiberglass industry, for example, NO_x emissions have been reduced from 4.5 lb/ton to 0.25 lb/ton (ADL, 1976). Data for the emissions from the glass industry are not available. However, the emissions are estimated to be less than 1.0 lb/ton of glass. The NO_x emissions from the power boiler are increased to 6.14 lb/ton of glass due to the increased use of electricity.

Process Option 5 - Batch Agglomeration/Preheating Alternative--

Batch preheat is an energy-conserving technology relating to a furnace modification rather than a method of furnace heating. Hence, this technology is applicable to all of the previously discussed methods of heating except for electric heating. The details of the process are given in Volume XI, page 58.

By improving the thermal efficiency of the furnace, this technology reduces the fuel requirement per ton of glass, thereby reducing the exhaust volume from the glass melting furnace. The reduction in gas volume correspondingly reduces NO_x emissions. The gas flow rate is decreased by about 20% and therefore the NO_x emissions are reduced by about 20% to approximately 6.4 lb/ton of glass. The NO_x emissions from the power boiler are comparable to those from the base case process, about 0.15 lb/ton of glass.

Summary

The NO_x emissions from the base case process and the selected processes are summarized in Table 12. In general, NO_x emissions from the furnace remain essentially the same, except in the case of the COHOGG process alternative. In the electric furnace alternative, there is a shift in the source of NO_x emissions from furnace to power boiler. The NO_x emissions from the glass furnace are not controlled and no cost-effective control technology currently exists.

COPPER INDUSTRY

Base Case Process - Conventional Copper Smelting

Conventional smelting involves the smelting of sulfide concentrates in the reverberatory furnace either directly or after roasting. The mixture

TABLE 12. ESTIMATED NO_x EMISSIONS FROM GLASS FURNACES
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	Estimated emission factor ($lb\ NO_x$/ton of glass) Process	Boiler	Total	Change from base case	NO_x emissions* (10^6 lb/yr) 1974**	1989-1974*
Base case: Natural gas firing	8.0	0.15	8.15	0	236	106
• Coal gasification	∿ 8.8	0.15	8.95	+ 0.8	--	116
• Direct coal firing	10.0	0.15	10.15	+ 2.0	--	132
• Coal-fired, hot gas generation	11.2	0.15	11.35	+ 3.2	--	148
• Electric melting	< 1.0	6.14	7.14	- 1.01	--	93
• Batch preheat with natural gas firing	∿ 6.4	0.15	6.55	- 1.6	--	85

* Based on increment in production from 1974 to 1989 - 13 million tons/year.

** Estimated 1974 emissions, if all plants emit 8.15 lb of NO_x/ton of glass are $8.15 \times 29 \times 10^6 = 236 \times 10^6$ lb/year.

of molten sulfides from the reverb is converted to blister copper in converters. A detailed description of this process is given in Volume XIV, page 23.

Large volumes of gas are produced in the reverberatory furnace and converter. NO_x emissions data from these sources or from alternative processes are not available. However, approximate estimates have been developed based on comparison with other processes.

The melting temperature of the matte in the reverberatory furnace is 2,000°F. The average gas temperature in the reverberatory furnace is 2,250°F, varying from 2,100°F to flame temperature. There is about 100% excess air. Temperature distribution in the furnace is not uniform, and therefore NO_x formation may be promoted except that reducing conditions are present. The NO_x concentration in the flue gas from the long dry cement kiln operating at an average temperature of 2,400°F, with 100% excess air, and nonuniform temperature distribution is 150 ppm (Volume X, page 58). The gas flow rate from the reverberatory furnace is 82,000 scfm (Volume XIX, page 26) and the smelter capacity is 100,000 tons of anode copper/year. Therefore, assuming 150 ppm NO_x concentration in the flue gas from the reverberatory furnace, we estimate the emissions to be equivalent to 7.85 lb of NO_x/ton of copper.

The melting point of the copper is 2,129°F and the average operating temperature of the converter is 2,300°F. Air is blown through the metal for oxidation. The temperature distribution in the gas phase is very uniform. NO_x emissions from the converter are again not available, but may be estimated by comparing it with other processes. The NO_x concentration in flue gas from a fluidized bed in the cement industry operating at 2,400°F uniform temperature and high excess air is 45 ppm (Volume X, page 58). The gas flow rate from the converter is 38,800 scfm (Volume XIV, page 26), assuming that all acid plant tail gas is from the converter and that smelter capacity is 100,000 tons of anode copper/year. Therefore, assuming 45 ppm NO_x concentration in the flue gas from the converter, we estimate emissions to be equivalent to 1.11 lb of NO_x/ton of anode copper.

Both types of roasters (multiple hearth and fluidized bed) usually operate at around 1,200°F. We expect that NO_x concentration in the gas from the roaster will be very low.

The estimated emission factor based on the above method is 7.85+1.11= 8.96 lb of NO_x/ton of copper from the process. The electricity consumed in conventional smelting varies from 347 kWh/ton in green feed smelting to 441 kWh/ton in calcine smelting. This will result in emissions at the power boiler equal to 2.73 to 3.47 lb of NO_x/ton of anode copper.

Process Option 1 - Outokumpu Flash Smelting Process Alternative--

The flash smelting alternative combines the separate roasting and smelting operations of conventional copper extraction into one combined roasting/smelting process. The major advantages of the method are a reduction in fuel used for smelting and production of a gas stream having a concentration of SO_2 which is suitable for sulfuric acid manufacture. A detailed description of the process is given in Volume XIV, page 41.

A direct oil-fired rotary kiln is used to dry the charge thoroughly before it is fed to the concentrate burner. The NO_x concentration in the flue gas from the kiln should be comparable to the NO_x concentration in the flue gas from the wet kiln in the cement industry. However, the gas flow rate per ton of feed should be higher in the cement kiln, because there the material is not only dried but preheated, calcined, and sintered. As an approximation, the difference in energy consumption in the wet and dry kilns in the cement industry may be assumed to be equal to the energy required for drying. This is roughly 20 to 50% of the energy consumed in the kiln (Volume X, page 98). Some 1.6 tons of feed to the cement kiln is required per ton of cement. The concentration of copper in the feed is only 15 to 30% and, therefore, 3 to 7 tons of feed to the kiln are required per ton of copper. The NO_x emissions from the wet cement kiln are 2.6 lb/ton of cement. Consequently, the emissions from the kiln in the alternative process are estimated at 2.6 lb of NO_x/ton of anode copper.

The gas temperature in the concentrate burner is about 2,500°F and the oxygen concentration in the flue gas is about 0.5%, but it may be as high as 2%. Conditions in the burner are reducing, as was the case in the conventional reverberatroy furnace. The NO_x concentration in the flue gas should be low. The NO_x concentration in the flue gas from a cement kiln (Volume X, page 58) operating at 2,400°F and low excess air is 45 ppm. The NO_x concentration in the flue gas from the concentrator may be on the same order (operating at reducing conditions but at a slightly higher temperature). Using a gas flow rate from the concentrator of 55,000 scfm (based on 100,000 tons of anode copper/year), the emission rate from the concentrator is estimated as 1.58 lb of NO_x/ton of anode copper.

The emissions from the converter in the flash smelting alternative would be comparable to or less than the emissions from the converter in the base case process, because the gas volume may be reduced due to the high grade matter (Volume XIV, page 43). Emissions from the converter in the base case process are 1.11 lb of NO_x/ton of anode copper.

The total emissions from the flash smelting process alternative are estimated at approximately 5.3 lb of NO_x/ton of anode copper. The NO_x emissions from the power boiler are estimated at 2.88 lb of NO_x/ton of anode copper (based on 366 kWh/ton of anode copper, Volume XIV, page 52).

Process Option 2 - Noranda Process Alternative--

The Noranda process combines in a single reactor the three operations of roasting, smelting, and converting of copper concentrates. The heat losses suffered during the transfer of concentrate from the roaster to the reverberatory furnace are suppressed as well as those occurring during the transfer of the matte from the reverberatory furnace to the converter. A detailed description of the process is given in Volume XIV, page 55.

The gaseous emissions from the Noranda process include 55,000 scfm from the acid plant (based on 100,000 tons of anode copper/year, Volume XIV, page 61). The acid plant tail gas includes 75% dilution air (Volume XIV, page 60). Therefore, the gas flow from the reactor is 31,500 scfm and contains 7.5% oxygen (Volume XIV, page 56). The reactor operates on air (without enriching with oxygen). Operating conditions favor NO_x formation (see the figure in Volume XIV, page 56). The NO_x concentration in the reactor flue gas would be comparable to the NO_x concentration of 150 ppm in the flue gas from a long dry cement kiln having 7.5% oxygen (Volume X, page 58). Thus, the NO_x emissions are estimated at 3.0 lb of NO_x/ton of anode copper.

The NO_x emissions from the power boiler are the same as in the Outokumpu flash smelter process, 2.88 lb of NO_x/ton of anode copper.

Process Option 3 - Mitsubishi Process Alternative--

The Mitsubishi process consists of three metallurgical stages, each of which is carried out in a separate furnace. Thus, there is a smelting furnace for concentrates, a converting furnace to oxidize iron in the matte and make blister copper, and a slag-cleaning furnace. Intermediate products in the molten state move continuously among the respective furnaces which are thus functionally connected with each other. A detailed description of the Mitsubishi process is given in Volume XIV, page 71.

The total gas flow rate from the smelting, slag-cleaning, and converting furnaces is 55,000 scfm (based on 100,000 tons of anode copper/year). Oxygen is used to enrich the air in this process. The operating temperatures and the breakdown of gas flow rates from individual furnaces are not reported, and therefore, NO_x emissions cannot be estimated but will probably be of the same order of magnitude as in the Noranda or Outokumpu processes namely about 3 to 5 lb NO_x/ton copper.

The emissions from the power boiler are comparable to those from the power boiler for the Outokumpu flash smelting process--about 2.88 lb of NO_x/ton of anode copper.

Process Option 4 - The Use of Oxygen in Smelting--

Copper smelting can be conducted with pure oxygen or by using oxygen-enriched air. An increase in oxygen concentration will result in higher process temperatures. A detailed description is given in Volume XIV, page 82. The specific example selected for examination is Outokumpu

flash smelting. Oxygen enrichment results in the reduction of emission volume; however, the operating temperatures are generally increased.

Also, the total NO_x formation rate is increased (Volume XIV, page 84). The emission rates due to oxygen enrichment in this alternative cannot be estimated due to the limited data.

If pure oxygen is used, then NO_x emissions are reduced to zero, except those formed due to nitrogen in the fuel and fuel materials.

Process Option 5 - Arbiter Process--

The Arbiter process is a hydrometallurgical leaching process (discussed in Volume XIV, page 95-106). NO_x process emissions are estimated to be neglible. However, 2.5 tons of oxygen and 3,000 kWh of electric energy are used per ton of copper. Since oxygen generation requires about 360 kWh/ton of oxygen, total electric energy requirements are 3,900 kWh/ton copper (=3000 + 2.5 x 360). Thus, NO_x emissions from the power boiler are estimated to be 30.71 lb per ton of copper. In addition, 20,000 lb of purchased steam are required. If we assume that low pressure process steam for the Arbiter process is obtained as a byproduct from the power boiler, there would, of course, be no incremental NO_x emissions, since more than enough steam is available. (If the steam is generated from a separate on-site boiler, additional NO_x emissions will be created from raising 20,000 lb of process steam requiring 1.22×10^6 Btu of fuel/1000 lb of steam (Volume II, page 17). These NO_x emissions are calculated to be 18.3 lb/ton copper, based on 0.75 lb of NO_x emissions per million Btu.)

Summary

The NO_x emissions from the base case copper smelting process and the selected alternative processes are summarized in Table 13. The use of oxygen-enriched air in furnaces is not included in the summary table because emission data from the oxygen enrichment alternative are not available. The recovery of slag alternative (Volume XIV, page 85) is also not included in the summary table because it has no NO_x emissions. The alternative processes for smelting reduce NO_x emissions by 30-50 percent. The NO_x emissions from the Mitsubishi process are not available but would probably be lower than those from the base case process. These estimates are based on comparison with other processes and, therefore, represent first approximations only.

FERTILIZER INDUSTRY

Base Case Process - Nitric Acid Industry Without NO_x Emission Control

The base case process in the nitric acid industry was a process with no NO_x emission control. Nitric acid is produced by oxidation of ammonia in a reactor, usually under high pressure and high temperature over a platinum catalyst, forming nitric oxide. The gaseous products from the reactor and oxygen are cooled to form NO_2 and are sent to an absorption tower to form the acid product. In the pressure process (base case

TABLE 13. ESTIMATED NO_x EMISSIONS - COPPER SMELTING
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	Estimated emission factor (lb NO_x/ton of anode copper) Process	Power boiler	Total	Change from base case	NO_x emissions* (10^6 lb/yr) 1974**	1989-1974*
Base case: Conventional smelting	∿ 9.0	2.7-3.5	∿12	0	19.4	13
• Outokumpu flash smelting	∿ 5.3	2.9	∿ 8.2	- 4	--	9
• Noranda process	∿ 3.0	2.9	∿ 5.9	- 6	--	6
• Mitsubishi process	∿3 to 5	2.9	∿ 6-8	- 4 to 6	--	4-7
• Arbiter process	small	30.7	30.7	19	--	34

* Based on increment in production from 1974 to 1989 - 1.1 million ton/year.

** Estimated 1974 emissions, based on the emission factor of 12.1 lb of NO_x/ton of anode copper are $12.1 \times 1.6 \times 10^6 = 19.4 \times 10^6$ lb/year.

process), the gas is reheated for power recovery purposes and discharged to the atmosphere at 400-500°F. In the atmospheric system, tail gas discharged to the atmosphere is cold. The tail gas is reddish-brown. The intensity of the color depends on the concentration of nitrogen dioxide present. Concentrations of 0.13% to 0.19% and higher by volume of nitrogen dioxide produce a definite color in the exit plume. Effluent gas containing less than .03% nitrogen dioxide is essentially colorless.

Uncontrolled and controlled NO_x emissions from nitric acid plants are given in Table 14 and are shown in Figure 1. Emissions are in the range of 50-55 lb/ton of 100% acid. The tail gas from the pressure process may be considered to have the following average composition.

Total Nitrogen Oxides, $NO + NO_2$: 0.3%
Oxygen: 3%
H_2O: 7%
Nitrogen: Balance.

In the pressure process, steam is generated from the tail gas, and therefore emissions at the power boiler are reduced by 0.53 lb of NO_x/ton of acid, provided this steam is used elsewhere in the plant.

In the United States, the limits on nitric oxide and nitrogen dioxide (commonly considered together as NO_x) emitted from nitric acid plants are 3 lb/ton of 100% acid for new plants (Federal standard) and 5.5 lb/ton of 100% acid on the average (state standards) for old plants (Volume XV, page 29). This is equivalent to approximately 200 and 400 ppm, respectively, by volume in the tail gas.

Process Option 1 - Catalytic Reduction Process Alternative--

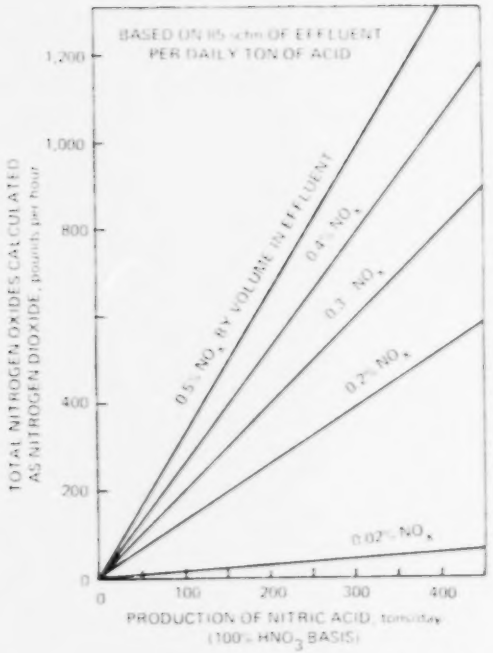
In the catalytic reduction process, the residue tail gas from the absorber, essentially nitrogen, is demisted and then reheated with steam. The hot tail gas is then further heated by passing it through the shell side of the heat exchanger train utilized to cool the hot process gas.

Before being introduced into the hot gas expander, the reheated tail gas is passed through a chamber that contains a catalyst. The oxides of nitrogen are reduced to N_2 and O_2 in the combustor. Natural gas or hydrogen is used as a fuel. A detailed description of the process is given in Volume XV, page 33. The stack effluent is usually clear and colorless, indicating reduction in all nitrogen dioxide to nitric oxide at least to less than 300 ppm. The emission factor is less than 7 lb of NO_x/ton of acid and varies with the fuel used in the combustor, as shown in Table 15. Part of the energy consumed in the combustor is recovered in the expander. Therefore, as in the base case process, emissions at the power boiler are reduced by 0.87 lb of NO_x/ton of acid, provided the steam generated is used elsewhere in the plant.

TABLE 14. ESTIMATED NO_x EMISSIONS FROM NITRIC ACID PLANTS

Process	Control efficiency (%)	Emission (ppm in flue gas)	NO_x (lb/ton)*
Uncontrolled	0	3,000	50-55
Catalytic reduction (natural gas-fired)	78-97	200-300	2-7
Catalytic reduction (hydrogen-fired)	97-99.8	0-100	0-1.5
Catalytic reduction (75% hydrogen, 25% natural gas)	98-98.5	45-65	0.8-1.1
Molecular sieve method	> 98.5	< 50	< 0.9
Extended water absorption (Grande Paroisse)	> 93	< 200	< 3.5
CDL/Vitok process	> 94	< 175	< 3.0
Masar process	93-97	100-200	1.75-3.5
NaOH-water absorber	91	270	4

*Based on 100% acid production.



Source: "Atmospheric Emissions from Nitric Acid Manufacturing Processes," USHEW, Publication No. 999 AP 27, 1966.

Figure 1. Total NO_x (Calculated as NO_2)/Hour vs Daily Production of Nitric Acid

Option 2 - Molecular Sieve Method Alternative--

This method is based on the principle of absorption, oxidation, and regeneration of the molecular sieve. An oil-fired heater is used to provide heat for regeneration. The process has high efficiency for removal of NO_x gases. The NO_x outlet concentration is generally below 50 ppm (0.9 lb of NO_x/ton of acid). A detailed description of the method is given in Volume XV, page 36.

Steam and electrical energy are used in the molecular sieve process. The estimated NO_x emissions generated from the power boiler are 0.22 lb/ton of acid.

Option 3 - Extended Water Absorption, or Grande Paroisse, Process Alternative--

In the extended water absorption, or Grande Paroisse, process, tail gas from the primary absorption tower which typically contains between 1,500 and 5,000 ppm NO_x is routed to the secondary absorber for additional extended absorption of NO_x. The tail gas is contacted countercurrently with the process water and additional acid produced in the secondary absorber is pumped to the primary absorber. A startup acid pump is included to circulate a large quantity of weak acid through the secondary absorber to fill the absorber tray as quickly as possible during startup. A detailed description of the process is given in Volume XV, page 37. The process may be used in a new plant, or may be retrofitted in an existing plant, and will meet the NO_x standard.

The estimated emissions from the Grande Paroisse process are 3.5 lb of NO_x/ton of acid (200 ppm NO_x in the flue gas). The emissions from the power boiler are 0.06 lb of NO_x/ton of acid.

Option 4 - CDL/Vitok Process Alternative--

This process uses the principle of scrubbing tail gas with nitric acid under conditions which reduce the nitrogen oxides to the desired level. Both physical absorption and stripping and chemical oxidation absorption are used. The reaction may be catalyzed in some applications to reduce the size of the equipment required. No chemicals other than water and nitric acid are required for the process, thus avoiding additional new waste disposal problems. The detailed description of the process is given in Volume XV, page 38. The NO_x content in the tail gas is less than 3 lb/ton of nitric acid (175 ppm NO_x in the flue gas). The emissions from the power boiler are estimated at 0.21 lb of NO_x/ton of acid.

Option 5 - Masar Process Alternative--

The Masar process, as applied to nitric acid plants, takes the tail gas from the exit of the absorption tower and passes it through a gas chiller before it is cooled. During the cooling operation, condensation occurs with the formation of nitric acid. The chilled gas and condensate passes into the Masar absorber where additional NO_x is removed from the gas. A detailed description of the process is given in Volume XV, page 39. The

tail gas meets regulatory standards with regard to NO_x abatement. The NO_x in the exhaust tail gas from one operating plant has been reported to be between 100-200 ppm for a one-year period (1.75-3.5 lb of NO_x/ton of acid). The estimated emissions from the power boiler are 0.09 lb of NO_x/ton of acid.

The spent Massar solution contains urea and ammonium nitrate in the form of a weak solution. The solution can be utilized in preparing liquid fertilizers. Companies that do not make liquid fertilizers may sell the solution to companies that do or to farmers for direct application.

Option 6 - Alkali Scrubbing Process--

Alkaline scrubbers also reduce the emission of nitrogen oxides effectively. As reported in Volume XV, page 42, in the two-stage sodium hydroxide water scrubber, NO_x can be reduced by 91%. This method of control is used only if production of sodium nitrate is desirable.

Summary

The NO_x emissions from the base process and alternative processes are summarized in Table 15. All the NO_x control methods can be used to reduce the emissions to less than 5 lb/ton of nitric acid produced, or equivalent to 300 ppm of NO_x in the flue gas. (The emissions from the power boiler are small.) The economics, as reported in Volume XV, page 34, favor the CDL/Vitok and Masar processes. Also, the energy requirements in the extended water absorption, CDL/Vitok process, and the Masar process are reduced compared to energy consumed in the catalytic combustor. In general, the NO_x emissions are reduced by more than 90% in each of the above alternative processes.

AMMONIA

The base case technology is the production of ammonia, based on steam reforming, using natural gas as the feedstock. In the alternative processes, ammonia is produced via coal and heavy oil feedstocks.

Base Case Process: Ammonia Production Based on Gas Feedstock

The four major operations in the manufacture of ammonia include: gas preparation, hydrogen production, gas purification, and ammonia synthesis. Gas preparation is typically done by steam reforming of natural gas to produce carbon monoxide and water. In the second step, the product gases are catalytically shifted to carbon dioxide and hydrogen, and the carbon dioxide is removed from the gas stream. Ammonia is then synthesized by the reaction between hydrogen and nitrogen (produced from atmospheric air) at elevated temperatures and pressures in the presence of a catalyst. The ammonia synthesis loop purge gas is recycled to the reformer where it is burned with natural gas fuel. A detailed description of the base case technology is presented in Volume VII, page 25.

TABLE 15. ESTIMATED NO_x EMISSIONS - NITRIC ACID INDUSTRY
BASIS: NO_x ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	Estimated emission factor (lb/NO_x/ton of acid) Process	Power boiler	Total	Change from base case	NO_x emissions* (10^6 lb/yr) 1974**	1989-1974*
Base case: Uncontrolled NO_x emissions	52.5	- 0.5	52.0	-	426	343
• Catalytic combustor						
Natural gas-fired	5	- 0.9	4.1	- 47.9	--	27
Hydrogen-fired	∿ 1	- 0.9	0.1	- 51.9	--	0.7
75% hydrogen 25% natural gas	∿ 1	- 0.9	0.1	- 51.9	--	0.7
• Molecular sieve	∿ 0.9	0.2	1.1	- 50.9	--	7.3
• Grande Paroisse	∿ 3.5	0.1	3.6	- 48.4	--	24
• CDL/Vitok	∿ 3.0	0.2	3.2	- 48.8	--	21
• Masar	∿ 2.5	0.1	2.6	- 49.4	--	17.2

* Based on the incremental production of acid from 1974 to 1989; 6.6×10^6 tons.

** The NO_x emissions based on the emission factor of 52.0 lb/ton of acid in the year 1974 are $52.0 \times 8.2 \times 10^6 = 426.4 \times 10^6$ lb.

Process fuel requirements include 12.6 MM Btu/ton of natural gas which is used to fire the steam reformer (Volume VII, page 27). Steam is generated by heat recovered from the flue gas leaving the primary reformer and from the process gas leaving the secondary reformer. Auxiliary gas-fired boilers are used to generate steam only during startup. Power requirements are estimated at 95 kWh/ton of ammonia (Volume VII, page 27).

NO_x emissions from the natural gas-fired reformer--based on the emissions factor of 0.29 lb/10^6 Btu of natural gas--are estimated to be 0.95 lb/ton of ammonia. This emissions factor includes NO_x from the natural gas utilized as fuel for the reformer and includes NO_x gas used as feedstock, since the ammonia synthesis loop purge gas which contains the NO_x from the feedstock is burned in the primary reformer.

NO_x emissions from the coal-fired power boiler are estimated to be 0.36 lb/ton of ammonia.

Process Option 1 - Ammonia Production Based on Coal Gasification--

Synthesis gas for ammonia production is obtained from the coal feedstock by freeing the hydrogen that is present in the coal and by reacting the carbon in the coal with steam to produce additional hydrogen and carbon monoxide. As in the base case process, the synthesis gas is shifted to a hydrogen and carbon dioxide product; the gases are purified; and ammonia is synthesized from nitrogen and hydrogen gases. The details of this process option are described in Volume VII, page 37.

An auxiliary coal-fired boiler is required for this process alternative. Fuel requirements (coal) are estimated at 5.22×10^6 Btu/ton of ammonia. In addition, electrical power requirements have been estimated to be 1.70×10^6 Btu/ton, equivalent to 162 kWh/ton (Volume VII, page 95).

NO_x emissions from the auxiliary boiler, based on the emission factor of 0.75 lb/NO_x x 10^6 Btu, are estimated to be 3.92 lb/ton. In addition, NO_x is also produced during gasification from the nitrogen contained by the coal. Since about 1.33 tons of coal feedstock are required per ton of ammonia (equivalent to 28.9×10^6 Btu/ton of ammonia), then NO_x emissions are estimated at 21.68 lb/ton of ammonia.

NO_x emissions from the coal-fired power boiler are estimated at 1.28 lb/ton of ammonia.

Process Option 2 - Production of Ammonia from Heavy Fuel Oil--

In the production of ammonia from heavy fuel oil, synthesis gas is produced from the fuel oil by the partial oxidation and steam reformation of the hydrocarbon. The carbon monoxide and steam in the product gases is subsequently reacted catalytically to produce additional hydrogen. The acid gases, carbon dioxide, and other impurities are removed from the hydrogen stream. Ammonia is finally synthesized from the hydrogen and nitrogen. An air separation plant supplies nitrogen for the ammonia synthesis step,

and oxygen for the partial oxidation of the fuel oil. This process option is described further in Volume VII, page 67.

Residual oil feedstock requirements are estimated to be about 4.27 bbl/ton of ammonia. Process fuel requirements which include fuel oil and naphtha are estimated to be approximately 7.26×10^6 Btu/ton of ammonia (Volume VII, page 71).

Resulting NO_x emissions from the feedstock and fuel, based on an emissions factor of 0.33 lb/10^6 Btu of oil, are estimated to be 11.28 lb/ton of ammonia.

These NO_x emissions result during both the combustion of the fuel oils and the gasification of the feedstock.

Power requirements for this process are estimated to be 103 kWh/ton (Volume VII, page 71). NO_x emissions from the power boiler are estimated to be 0.81 lb/ton of ammonia.

Summary

The estimated NO_x emission factors for the base case and alternative processes are summarized in Table 16. NO_x emissions created by the production of ammonia from coal and heavy fuel oil are estimated to be, respectively, over 170% and 20% greater than the NO_x emissions from the base case. This increase is presumably a result of the higher nitrogen content of the coal and heavy fuel oil.

IRON AND STEEL

Recovery of Carbon Monoxide from BOP Vessels

Base Case Process - Complete Combustion System--

The base case process is a complete combustion system. The gases issuing from the mouth of the furnace are collected in a hood with a considerable infiltration of air, burned in the hood, and cooled and cleaned of particulates before being released to the atmosphere. Approximately $.88 \times 10^6$ Btu of heat/ton of steel are lost to the atmosphere (Volume III, page 26). A detailed description of this system is presented in Volume III, page 18.

It is estimated that 0.26 lb of NO_x is produced/ton of steel by the combustion of the BOP vessel off-gasses. This estimate is based on the assumption that the NO_x formation during carbon monoxide combustion is approximately 0.29 lb/10^6 Btu, i.e., the amount produced during the combustion of natural gas. (NO_x emissions from BOP off-gas combustion are not given in either Volume III or in AP 42.)

The combustion system consumed 14 kWh of electricity/ton of steel; this electricity is required for the operation of the gas scrubber system. NO_x emissions from the power boiler are estimated at 0.11 lb/ton of steel.

TABLE 16. ESTIMATED NO_x EMISSIONS - AMMONIA INDUSTRY
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	Estimated emission factor ($lb\ NO_x$/ton of ammonia) Process	Power boiler	Total	Change from base case	NO_x emissions* (10^6 lb/yr) 1974**	1989-1974*
Ammonia production based on						
Base case: Natural gas	9.57	0.36	9.93	--	91	127
• Coal gasification	25.6	1.28	26.88	+ 16.95	--	344
• Heavy fuel oil	11.28	0.81	12.09	+ 2.16	--	155

* Based on increment in production from 1974-1989 of 12.8×10^6 ton/year.

** Estimated 1974 emissions, based on the total emission factor of 9.93 lb of NO_x/ton of ammonia are $9.93 \times 9.2 \times 10^6 = 91 \times 10^6$ lb/year.

Alternative Process: Non-Combustion BOP Off-Gas Recovery System--

In the alternative process, carbon monoxide is collected and recovered from the BOP off-gas. Approximately one-half of the carbon monoxide (0.44×10^6 Btu/ton of steel) is recovered; the remainder is flared (Volume III, page 26). Two recovery systems, the OG process and the IRSID-CAFL process, and discussed in Volume III, page 19-22. About 0.13 lb of NO_x is produced/ton of steel during the flaring of the unrecovered off-gases. The OG process, non-combustion system, consumes about 8 kWh of electricity/ton of steel (Volume III, page 26). Energy consumptions are less than those for the combustion system as a result of the lower gas volumes handled. NO_x emissions from the power boiler are estimated to be 0.06 lb/ton of steel.

Blast Furnace

Base Case Process - Desulfurization Hot Metal in the Blast Furnace--

The base case system is considered to include a blast furnace, cyclone, and venturi scrubber. The sulfur content of the blast furnace gas is completely controlled by adding limestone to form the sulfur-bearing slag and by limiting the sulfur content of the metallurgical coke. This process is further discussed in Volume III, page 29.

NO_x emissions from the process have not been estimated in Volume III. Power requirements are estimated to be 46 kWh/ton of hot metal (Volume III, page 41). Estimated emissions from a coal-fired power boiler are 0.36 lb of NO_x/ton of hot metal.

Process Option 1 - Blast Furnace with External Desulfurization--

Addition of an external desulfurization tip is an alternative method of controlling the sulfur content of blast furnace hot metal. External desulfurization is achieved by injecting sulfur-reacting reagents (e.g., calcium or magnesium compounds carried in an inert gas such as nitrogen) into high-sulfur, hot metal from a blast furnace. These compounds form a sulfide slag that is skimmed off prior to charging the hot metal to the BOP. Use of external desulfurization either permits limestone and coke ratios to be reduced, or allows the sulfur content of the coke to be increased without increasing the limestone charge to the furnace. A detailed description of thie process is given in Volume III, page 31.

NO_x emissions from the blast furnace have not been estimated in Volume III. Electricity consumption in this alternative process is the same as the base case process, so power boiler emissions estimates are also the same.

Quenching of Coke

Base Case Process - Wet Quenching--

In the base case process, the hot coke is pushed from the oven into a coke car where it is quenched with water. Steam which is produced is

vented to the atmosphere. Excess water is allowed to drain and is often recirculated.

Electricity consumed by the wet quenching process is not estimated in the study presented in Volume III.

Process Option 1 - Dry Quenching--

In dry quenching of coke, the hot coke pushed from the ovens is cooled in a closed system. "Inert" gases extract heat from incandescent coke by direct contact. The heat is then recovered from the inert gases in a waste heat boiler or by other techniques. The incremental electrical requirements are estimated at 8.4 kWh/ton of coke. Incremental emissions from the power boiler are estimated at 0.07 lb of NO_x/ton of coke. In addition, the recovered heat, estimated at 1.1×10^6 Btu (105 kWh) per ton of coke may be used to generate electricity. A credit for NO_x emissions which would otherwise be produced from a coal-fired power boiler is estimated to be 0.83 lb of NO_x/ton of coke. Thus, the net incremental emissions credit is estimated to be 0.76 lb of NO_x/ton of coke.

Steel-Making

Base Case Process - Coke Oven, Blast Furnace (BF), and Basic Oxygen Furance (BOF) Route for Steel-Making--

The base case process is the conventional process for steel-making. For our analysis we assumed that 30% scrap metal would be used in the BOP. A detailed description of the process is given in Volume III, page 54.

Electricity consumed by the coke oven, BF, BOF, and pollution control equipment is estimated at 120 kWh/ton of steel (Volume III, page 79, 82-84). NO_x emissions from the power boiler are estimated at 0.95 lb/ton of steel.

Steam consumed by the coke-making facilities is required at about 670 lb/ton of steel. If this steam is generated with coal, then NO_x emissions are estimated at 0.65 lb/ton of steel.

Process Option 1 - Direct Reduction Route for Steel Making--

Iron oxide pellets, ore lumps, etc., can be partially reduced in the solid state by reaction with a reducing gas mixture. These prereduced materials can partially or entirely replace purchased scrap in the steel-making electric arc furnaces. In this alternative process, it was assumed that 30% scrap is used with 70% prereduced pellets to make steel. A detailed process description is given in Volume III, page 54.

Electricity consumed by the sponge iron facilities, the electric furnace shop, and the pollution control equipment is estimated at 712 kWh/ton of steel. NO_x emissions from the coal-fired power boilers are estimated at 5.6 lb/ton of steel.

Summary

The emissions factor and total emissions for the base processes and the alternative processes are summarized in Table 17. In the basic oxygen process, recovery of off-gas from the BOF offers a 50% reduction in NO_x emissions, since only one-half of the off-gases is flared. In the production of iron, external desulfurization offers no reduction in NO_x emissions from the base case process.

Steel-making by the direct reduction method will result in nearly a three-fold increase in emissions over the conventional route because of the higher power requirements of direct reduction process.

PHOSPHORUS/PHOSPHORIC ACID

Phosphoric Acid Production

Base Case Process - Electric Furnace Production of Phosphorus and Conversion of Phosphorus to Phosphoric Acid--

In this process, phosphate rock is reduced to elemental phosphorus by coke in an electric furnace. Phosphorus vapor and carbon monoxide are produced. The phosphorus is condensed and subsequently converted to pure phosphoric acid. The details of this process are presented in Volume XIII, page 23-24.

Electric furnace production of phosphorus is a very energy-intensive operation. Electrical energy requirements are estimated at 13,000 kWh/ton of phosphorus (P_4). More than 90% of this energy is required by the furnace; the remainder is required for pumping operations. In addition, 1.9 tons of coke/ton of P_4 are charged to the furnace, where carbon monoxide is produced. The carbon monoxide is recovered and fired in the rotary kiln where the furnace feed materials are prepared. Natural gas (6×10^6 Btu/ton of P_4) is required to supplement the carbon monoxide gas (Volume XIII, page 33).

NO_x emissions from the electric arc furnace have not been quantified in either Volume XIII or in AP 42; these emissions are assumed to be negligible.

NO_x is produced by the combustion of natural gas and carbon monoxide in the rotary kiln; emissions are estimated to be 2.76 lb/ton of P_2O_5 (6.3 lb/ton of P_4). The NO_x emission factor for carbon monoxide combustion was not available from either Volume XIII or AP 42 (EPA, 1975). However, it was expected that NO_x production during carbon monoxide combustion would be similar to NO_x production during natural gas combustion; hence, the emission factor, 0.29 lb of $NO_x/10^6$ Btu of gas, was used for both fuels.

NO_x emissions from the coal-fired power boiler are estimated to be 45 lb/ton of P_2O_5 (103 lb/ton of P_4).

TABLE 17. ESTIMATED NO_x EMISSIONS - IRON AND STEEL INDUSTRY
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	NO_x estimated emission factor (lb/ton of product)			Change from base case	Incremental NO_x emissions for 1974 - 1989*	
	Process	Power boiler	Total		1974**	1989-1974*
Base case: BOP with no off-gas recovery	0.26	0.11	0.37	--	30	22
• BOP with off-gas recovery	0.13	0.06	0.19	- 0.18	--	11
Base case: Blast furnace (BF)	--	0.07	0.07	--	7	3
• Blast furnace with external desulfurization	--	0.07	0.07	0.0	--	3
Base case: Wet quenching of coke	0.0	NA†	NA	--	NA	NA
• Dry quenching of coke	- 0.83††	0.07††	- 0.76††	- 0.76††	NA	- 21††
Base case: Steel-making						
• Coke oven, BF, BOP route	0.8	1.0	1.8	--	148	108
• Direct reduction EAF route	--	5.6	5.6	3.8	--	336

(continued)

TABLE 17. (continued)

* Estimated 1974 emissions (based on the emission factor of 0.07 lb/ton of iron) are $0.07 \times 100 \times 10^6 = 7 \times 10^6$ lbs from iron production; estimated 1974 emissions based on the emission factor of 0.37 lb/ton of BOP steel, are $0.37 \times 82 \times 10^6 = 30 \times 10^6$ lb; and estimated 1974 emissions, based on emission factor of 1.8 lb NO_x/ton of steel from coke oven, blast furnace, BOP route, are $1.8 \times 82 \times 10^6 = 148 \times 10^6$ lb.

** Based on increment in production from 1974-1989 -- 27.8×10^6 tons of coke, 44.8×10^6 tons of iron, and 60×10^6 tons of steel.

† NA = not available

†† Emission factor is based on incremental requirements of the dry quench process as it compares to the wet quench process.

Process Option 1 - Wet-Process Phosphoric Acid with Chemical Cleanup--

In the wet process, phosphate ore is reacted with sulfuric acid. Phosphoric acid (32% solution) is recovered from the undigested ore and the gypsum byproduct. This acid is concentrated by evaporation to the 54% P_2O_5 product. The wet process is more completely described in Volume XIII, page 35-37. There are a number of impurities in wet-process phosphoric acid which make it unsuitable for use in certain applications. Wet acid is purified to sodium tripolyphosphate by a two-stage neutralization process (Volume XIII, page 49).

Steam is required to concentrate the acid solution. Steam may be generated by oil, or if the phosphoric acid plant is integrated with a sulfuric acid plant, then this steam may be generated from heat released by the oxidation of sulfur. About 13 million Btu/ton of P_2O_5 is recovered; approximately half of the steam heat is used in the sulfuric acid plant, and the other half is used by the phosphoric acid plant.

If the phosphoric plant is not integrated with a sulfuric acid plant and the steam is generated from oil, then NO_x emissions are estimated to be 2.52 lb/ton of P_2O_5.

Electricity (250 kWh/ton of P_2O_5) is required to drive pumps, agitators, and filters in the wet-acid process. An additional 16 kWh/ton of P_2O_5 is required for the chemical cleanup of the acid (Volume XIII, page 57). NO_x emissions from a coal-fired power boiler are estimated to be 2.10 lb/ton of P_2O_5.

Wet-Process Phosphoric Acid with Solvent Extraction Cleanup--

This method of wet-process phosphoric acid cleanup is based on the fact that phosphoric acid can be transferred from solution in an aqueous phase to solution in an organic phase and leave behind undesirable impurities, such as calcium chloride, in the aqueous layer. The organic phase can then be contacted in a separate unit with fresh water to yield a pure solution of phosphoric acid. A detailed process description is given in Volume XIII, page 60.

The solvent-extraction process requires about 10,000 lb of steam/ton of P_2O_5 for concentration of the acid from 15% as it is produced in the extraction section to a concentration of about 60% P_2O_5 (Volume XIII, page 70). If the steam is generated with fuel oil, the NO_x emissions are estimated to be 4.30 lb/ton of P_2O_5.

Electricity requirements for the solvent extraction process are about 300 kWh/ton of P_2O_5 (Volume XIII, page 70). The estimated NO_x emissions from a coal-fired power boiler are 2.36 lb/ton of P_2O_5.

Summary

The emissions factor and total emissions for the base case process and alternative processes are summarized in Table 18. Both of the process options offer a significant reduction in NO_x emissions over the base case

TABLE 18. ESTIMATED NO_x EMISSIONS - PHOSPHORUS/PHOSPHORIC ACID PRODUCTION
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	NO_x estimated emission factor (lb/ton P_2O_5)				NO_x emissions* (10^6 lb/yr)	
	Process	Boiler	Total	Change from base case	1974**	1989-1974*
Base case:						
Electric furnace	2.8	45.0	47.8	--	67	30.1
• Chemical cleanup of wet-process acid	2.5	2.1	4.6	- 43.2	--	2.9
• Solvent extraction of wet-process acid	4.3	2.4	6.7	- 41.1	--	4.2

* Based on the incremental production detergent grade phosphoric acid from 1974 to 1989 = 0.63×10^6 lb/yr.

** NO_x emissions based on the emission factor of 47.8 lb/ton of detergent-grade phosphoric acid in the year 1974 are $47.8 \times 1.4 \times 10^6 = 67 \times 10^6$ lb.

decrease. This reduction is primarily a result of the lower power requirements for wet-process phosphoric acid production.

TEXTILES INDUSTRY

Two textile mills, an integrated knitting mill and an integrated weaving mill, were examined. The mill operation includes the knitting of the greige yarn or the weaving of greige fabric and the subsequent dyeing and finishing of the fabric .

Knit Fabrics Production

Base Case Process--

In the knitting mills, yarn is knitted into fabric in the greige mill. The greige fabric is next scoured to remove knitting oil, before being dyed, washed, and spun dry to remove as much water as possible before hot-air drying. A finish (softener/lubricant) is applied to the fabric, which is then dried and heat-set. Details of the knitting mill operation are presented in Volume IX, page 33.

Natural gas is used for the hot-air drying and heat-set operations. It is unlikely that the natural gas will be supplemented, as it is required by all of the equipment presently available for fabric drying and heat-setting operations. NO_x emissions from these operations--based on the emissions factor of 0.29 lb of $NO_x/10^6$ Btu of natural gas--are estimated to be 2.42 lb/ton of fabric.

Steam is used for the heat input to the scouring, dyeing, and washing operations. In the base case process, it was assumed that the steam would be generated with low-sulfur residual fuel oil. Estimated NO_x emissions--based on the emission factor of .33 lb/10^6 Btu of oil burned in the boiler (EPA, 1973)--are estimated to be 2.65 lb/ton of fabric. Because of the relatively small energy requirements of textile mills, it seems unlikely that coal will be used as a fuel for steam production (Volume IX, page 41).

Electricity is required to provide mechanical energy to transfer fabric from the beginning to the end of the process line and for knitting the yarn into the fabric. Electrical requirements of 360 kWh/ton of fabric will result in NO_x emissions of about 2.84 lb of NO_x/ton of fabric.

Advanced Aqueous Processing--

The sequence of operation is similar to the base case, except that the hot air drier is replaced by an air/vacuum extractor, thereby reducing natural gas requirements and increasing electrical requirements. Secondly, the scouring, dyeing, and washing operations are modernized with more efficient equipment, so that steam requirements are reduced. Advanced aqueous processing is described in detail in Volume IX, page 535-537.

Natural gas is used for the heat-setting operation. NO_x emissions--based on the emissions factor of 0.29 lb/10^6 Btu of natural gas--are estimated to be 0.24 lb NO_x/ton of fabric.

Steam requirements of 3800 lb/ton of fabric will result in 1.25 lb of NO_x/ton of fabric if the steam is generated by fuel oil. Electrical requirements of 500 kWh/ton of fabric will result in controlled emissions at the power boiler of 3.94 lb of NO_x/ton of fabric.

Solvent Case--

Solvent systems are assumed for the scouring, dyeing, and finishing operations. The fabric is steam-stripped to remove residual solvent. Clean solvent is recovered by distillation with steam. Details of this solvent system are provided in Volume IX, page 37-41.

Natural gas is used for the heat-setting operation. NO_x emissions are estimated to be 0.24 lb/ton of fabric. Steam requirements of 2200 lb/ton of fabric will result in 0.73 lb of NO_x/ton of fabric. Electricity requirements of 240 kWh/ton of fabric will result in controlled emissions of 1.89 lb of NO_x/ton of fabric.

Woven Fabrics Production

Base Case Process--

The operations of woven fabric preparation, dyeing, and finishing involve a much longer processing sequence than knit fabrics. These steps are described in Volume IX. page 44.

Natural gas is used in the drying, setting, and curing operations. NO_x emissions are estimated to be about 4.34 lb/ton of woven fabric.

Steam (15 lb/ton of fabric) is used for process water heating in the dyeing, washing, and finishing steps. Steam generated by fuel oil will produce controlled emissions of about 9.9 lb of NO_x/ton of fabric. Electrical energy requirements are estimated at 580 kWh/ton of product This will result in controlled NO_x emissions of 4.57 lb/ton of fabric.

Advanced Process--

The advanced processing includes a polyvinyl alcohol (PVA) recovery loop which recycles concentrated PVA solution back to sizing and the hot water back to the desizing operation. Details of the advances case sequence are presented in Volume IX, page 49.

Natural gas is used in the drying, setting, and curing operations. NO_x emissions are estimated to be 1.47 lb/ton of fabric.

Steam requirements have been reduced to 6.4 lb/ton of fabric by reduction in overall process water use and recycling of wash waters. This steam generation will produce 4.22 lb of NO_x/ton of fabric if these emissions

are not controlled. Electrical requirements have been reduced to 300 kWh/lb of steam. This will result in NO_x emissions of 2.36 lb/ton of fabric.

Summary

The emissions factors and total emissions for the base case process and alternative processes for both knit and woven fabric production are summarized in Table 19.

Both alternative processes for knit fabric production offer a decrease in NO_x emissions. The advanced aqueous process shows a more modest decrease since electric power consumption for this alternative is higher than the base case. The solvent process shows a more pronounced decrease (58%) in NO_x emissions, since natural gas, steam, and electrical power consumption is lower than in the base case.

The alternative process for woven fabric production also offers more than a 50% reduction in NO_x emissions, since natural gas, steam, and electrical power consumption are only about 50% of what is consumed in the base case process.

PULP AND PAPER INDUSTRY

Chemical Pulp

Base Case Process - Kraft Pulping--

In the Kraft process, chemical pulp is produced by cooking the wood chips at an elevated temperature and pressure in a digester. When cooking is completed, the contents of the digester are forced into a blow tank. The major portion of the spent cooking liquor which contains the dissolved lignin is drained and the pulp enters the initial stage of washing. From the blow tank the pulp passes through the knotter where chunks of wood are removed. The pulp is then washed and bleached before being pressed and dried into the finished product.

It is economical to recover both the inorganic cooking chemicals and the heat content of the spent liquor which is separated from the cooked pulp in the blow tank. Heat recovery is accomplished by first concentrating the liquor to a level that will support combustion and then feeding it to a furnace (recovery boiler) where heat and chemical recovery take place.

Steam is produced by both process wastes and fossil fuel. Waste organic solids from the pulping process are burned in the recovery boiler, and wood bark from wood preparation operations are burned with the fossil fuel boilers. The steam is delivered from the boilers to the turbines which extract energy from the steam for electric power generation. The steam is then used predominantly in the pulping, bleaching, and chemical recovery operations.

TABLE 19. ESTIMATED NO_x EMISSIONS - TEXTILE INDUSTRY
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	NO_x estimated emission factor (lb/ton fabric)				NO_x emissions for 1974-1989 (10^6 lb/yr)	
	Process	Power boiler	Total	Change from base case	1974	1989-1974*
Knit fabric						
Base case:	5.06	2.84	7.90	--	2.5**	0.95
• Advanced case	1.49	3.94	5.43	- 2.47	--	0.65
• Solvent case	0.97	1.89	2.86	- 5.04	--	0.34
Woven fabric						
Base case:	14.24	4.57	18.81	--	39.5†	15.2
• Advanced case	5.69	2.36	8.05	-10.76	--	6.5

*Based on increment in production from 1974-1989 - 0.12×10^6 ton/year (knit fabric)
- 0.81×10^6 ton/year (woven fabric)

**Estimated 1974 emissions from knit fabric production based on the total emission factor of 7.90 lb of NO_x/ton of fabric are $7.90 \times 0.32 \times 10^6 = 2.5 \times 10^6$ lb.

†Estimated 1974 emissions from woven fabric production based on total emission factor of 18.81 lb of NO_x/ton of fabric are $18.81 \times 2.1 \times 10^6 = 39.5 \times 10^6$ ton/year.

Fossil fuels, which supplement the process waste fuels include natural gas, fuel oil, and a small amount of coal (Volume V, page 21, 44). In view of the relatively even distribution of gas and oil users, and in view of the uncertainty of the future availability of fossil fuels, it was assumed that fuel requirements would be satisfied by oil.

NO_x emissions are estimated to be 1.0 lb/air dry ton of pulp from the recovery furnace and an equal amount from the lime kiln (EPA, 1975). NO_x emissions from bark waste are estimated to be 10.0 lb/ton of bark (EPA, 1975 page 1.6-2). The NO_x emission factor for the Kraft process is estimated to be 5.1 lb/ton of pulp. This includes NO_x produced from the lime kiln and NO_x produced by steam generation in both the recovery boiler and the bark boiler. The emission factor for power generation, 0.5 lb/ton of pulp, is seen to add about 10% to the process emissions, resulting in a total emission factor of 5.6 lb NO_x/ton of pulp.

Process Option 1 - Alkaline-Oxygen Pulping Process Alternative--

The alkaline-oxygen (A-O) pulping process is receiving industry attention because of its potential for a non-sulfur cooking step, which would eliminate the air pollution due to sulfur compounds.

The steps in the alkaline-oxygen process include an alkaline treatment to soften the wood chips, mechanical disintegration, and treatment with oxygen under alkaline conditions to remove most of the lignin, followed by the last three stages of the conventional multistage bleaching sequence: chlorine dioxide, caustic extraction, and chlorine dioxide. (A detailed description of the process is given in Volume V, page 84).

Steam and power are produced in this alternative in the same manner as they were produced in the base case. The NO_x emissions from the lime kiln and steam generation are estimated at 3.8 lb/ton of pulp, and NO_x emissions from the power generation are estimated at 0.3 lb/ton of pulp.

Process Option 2 - Rapson Effluent-free Kraft Process Alternative--

A number of changes in the base case pulping process have been made to eliminate effluents. The modified process is called the Rapson effluent-free Kraft process. (It is described in detail in Volume V, page 93.)

Steam and power are produced in this alternative in the same manner as they were produced in the base case. The NO_x emissions from the lime kiln and steam generation are estimated at 3.0 lb/ton of pulp, and NO_x emissions from power generation are estimated at 0.2 lb/ton of pulp.

Newsprint Pulp

Base Case Process - Refiner Mechanical Pulping (RMP) Route for Newsprint Pulp--

RMP is a mechanical pulping process that is an improvement over the conventional groundwood process since wood chips, sawdust, and shavings from sawmills or plywood mills can be used as raw materials. The wood particles are reduced in a pressurized disc refiner which consists of two circular

metal plates that generally rotate in opposite directions. RMP pulp (80%) is used with Kraft pulp (20%) in newsprint paper production. (A detailed description of the RMP process is given in Volume V, page 60.)

Fuel requirements for the RMP process are estimated at 0.3×10^6 Btu/air-dried ton (ADT) of pulp (Volume X, page 60). Resulting NO_x emissions are estimated at 0.1 lb/ADT of pulp produced solely by the RMP process. If 80% of the pulp is produced by the RMP process and 20% of the pulp is produced by the Kraft process, then the NO_x emissions are estimated to be 1.1 lb/ADT for the process and 9.4 lb/ADT for the power boiler.

Power requirements for the RMP process are estimated at 1475 kWh/ADT of pulp (Volume X, page 60). Resulting NO_x emissions based on a coal-fired power boiler are estimated at 11.6 lb/ADT of newsprint pulp.

Process Option 1 - Thermo-Mechanical Pulping (TMP) Process Alternative--

The TMP process is similar to the base case process (RMP process), except the wood particles are preheated to 130°C for a short period and then reduced to fibers in a pressurized disc refiner. (A detailed process is given in Volume V, page 98.)

Fuel and power requirements for the TMP process are identical to the requirements for the RMP process; hence the NO_x emission factors are the same; i.e., 0.1 lb/ADT from the process and 11.6 lb/ADT from the power boiler. If 95% of the pulp is produced by the TMP process, then the NO_x emissions are estimated to be 0.4 lb/ADT for the process and 11.0 lb/ADT for the power boiler.

Process Option 2 - De-inking of Old Newsprint for Newsprint Manufacture--

The de-inking of old newsprint for newsprint manufacture is a well-established commercial practice. A detailed description of the process is given in Volume V, page 113. Fuel oil requirements for the de-inking process are estimated at 3.3×10^6 Btu/ADT; hence NO_x emissions are estimated to be 0.4 lb/ADT of newspaper pulp.

Power requirements are estimated at 280 kWh/ADT; hence NO_x emissions are estimated at 2.2 lb/ADT.

Summary

Estimated particulate emissions factors for the pulp and paper industry are shown in Table 20. In the chemical pulp industry, both alternatives to the Kraft process offer a means of NO_x reductions. The emissions in the alkaline-oxygen pulping alternative process are about 27% lower than for the base case process. The emissions in the Rapson process are about 43% lower than the base case process. These reductions in NO_x emissions from the base case process result from the reduction in steam and power consumptions.

TABLE 20. ESTIMATED NO_x EMISSIONS - PULP AND PAPER INDUSTRY
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	NO_x estimated emission factor (lb/ton of pulp)*			Change from base case	NO_x emissions* (10^6 lb/yr)	
	Process	Power boiler	Total		1974**	1989-1974**
Chemical pulp						
Base case: Kraft pulp†	5.1	0.5	5.6	--	90	97
• Alkaline-oxygen pulping	3.8	0.3	4.1	- 1.5	--	71
• Rapson effluent-free Kraft	3.0	0.2	3.2	- 2.4	--	55
Newsprint Pulp						
Base case: Refiner mechanical pulping††	1.1	9.4	10.5	--	41	17.9
• Thermo-mechanical pulping	0.4	11.0	11.4	+ .9	--	19.4
• De-inking of old newsprint for newsprint manufacture	1.1	2.2	3.3	- 7.2	--	5.6

* Air-dry basis.

** Based on increment in emissions from 1974-1989 = 17.3×10^6 tons of chemical pulp/year and 1.7×10^6 tons of newsprint pulp/year.

(continued)

TABLE 20. (continued)

† Estimated 1974 emissions (based on the total emission factor of 5.6 lb/ton of pulp) are $5.6 \times 16 \times 10^6 = 90 \times 10^6$ lb/year.

†† Estimated 1974 emissions (based on the total emissions factor of 10.5 lb/ton of pulp) are $10.5 \times 3.9 \times 10^6 = 41 \times 10^6$ lb/year.

In the newsprint pulp industry, NO_x emissions are the lowest for the de-inking process option. The RMP and TMP processes produced more than three times the amount of NO_x emissions generated by the de-inking process. This can be attributed to the higher fuel and power consumptions of the RMP and TMP processes. The RMP pulp has slightly lower NO_x emissions than the TMP pulp since the RMP pulp contains more pulp from the Kraft process.

CHLOR-ALKALI INDUSTRY

Chlorine and Caustic Production

Base Case Process - Graphite Anode Diaphragm Cell--

The graphite anote diaphragm cell was selected as a basis for judging the energy and environmental effects resulting from the process changes studies, i.e., conversion to modified anodes and conversion to modified diaphragms, both changes being aimed at energy conservation.

Chlorine and caustic soda are produced by the electrolysis of brine. In the diaphragm cell, chlorine is formed at the graphite anode, while sodium ions migrate through the cell diaphragm to the cathode where a dilute solution of NaOH is produced. A more complete description of this process is presented in Volume XII, page 21-25.

The electrolysis of brine is an energy-intensive process, requiring about 3,274 kWh/ton of chlorine. In addition, the plant requires 7,368 lb of low-pressure steam/ton of chlorine for caustic evaporation and brine heating. Steam is generated by natural gas and byproduct hydrogen. Based upon 1,100 Btu/lb of low-pressure steam and an 85% boiler efficiency, the fuel requirement is 9.15×10^6 Btu/ton of chlorine (Volume XII, page 27).

NO_x emissions from the coal-fired power boiler are estimated at 25.80 lb/ton of chlorine. NO_x emissions produced from the gas-fired steam generator--based on 0.29 lb of $NO_x/10^6$ Btu of fuel--are estimated to be 2.65 lb/ton of chlorine.

Process Option 1 - Dimensionally Stable Anode--

The dimensionally stable anode (DSA), constructed of titanium and coated with precious metal/rare earth oxides, offers numerous advantages over the graphite anode which result in power savings of up to 20%. The anode area and anode-cathode spacing of the DSA remain constant throughout use, thereby preventing increased voltage requirements over time. Additional characteristics of the DSA are presented in Volume XII, page 44-47.

The DSA diaphragm cell process requires 3,151 kWh and 6,402 lb of steam/ton of chlorine. Steam is generated by the byproduct hydrogen and natural gas. Approximately 7.94×10^6 Btu of fuel is required per ton of chlorine (Volume XII, page 46).

NO_x emissions from power generation are estimated at 24.83 lb/ton of chlorine. NO_x emissions from steam generation are estimated to be 2.30 lb/ton of chlorine.

Process Option 2 - Expandable DSA--

Cell power consumption can be reduced by decreasing the gap between the anode and the cathode. With the rigid DSA, a "working" space must be allowed in which to assemble the cell. The expanded DSA is constructed so that the electrodes can be moved inward after the cell is assembled. This reduced spacing results in a reduction of about 325 kWh/ton of chlorine compared to the rigid DSA configuration. This power savings reduces NO_x emissions by about 2.55 lb/ton of chlorine from the emissions estimated for the rigid DSA cells.

Process Option 3 - Polymer Modified Asbestos--

By replacing the conventional asbestos diaphragm by one which is polymer-treated and is baked into place on the cathode, power consumption can be reduced because diaphragm swelling does not occur. Electrical consumption may be reduced by as much as 280 kWh/ton if an extra wide anode is used. Thus, NO_x emissions are estimated to be 2.21 lb/ton of chlorine less than the emissions estimated for the rigid DSA cells with standard diaphragms.

Process Option 4 - Polymer Membranes--

Microporous teflon-type polymer membranes which would replace the asbestos diaphragm entirely are being developed. These would give an energy performance equivalent to the polymer-modified asbestos with the "entra-wide" anode. Hence, the NO_x emissions would be identical to those of Process Option 3.

Process Option 5 - Ion Exchange Membranes--

These membranes would separate the anode and cathode compartments of the cell and would allow the diffusion of sodium ions to the cathode, but would not allow the diffusion of hydroxyl ions to the anode. Thus, the ion exchange cell is capable of producing a 25 to 40% caustic solution, whereas the standard cell produces a 10% caustic solution.

Energy use for a DSA with an ion exchange cell producing 40% NaOH is 2,980 kWh and 1,466 lb of steam/ton of chlorine (Volume XII, page 59). Significantly less steam is required since a rather concentrated NaOH solution is produced directly from the cell. Steam is generated by natural gas and byproduct hydrogen. Approximately 1.81×10^6 Btu of gas fuel are required per ton of chlorine (Volume XII, page 59).

NO_x emissions from power generation are estimated to be 23.24 lb/ton of chlorine. NO_x emissions from steam generation are estimated to be approximately 0.52 lb/ton of chlorine.

Process Option 6 - Mercury Cells--

Chlorine and caustic may also be produced in a mercury cell. In this type cell, brine flows through a slightly sloped trough. At the dimensionally stable anodes, located at the top of the trough, chlorine is produced. A dilute sodium amalgam is produced at the cathode (a thin layer of mercury which flows along the bottom of the trough). A 50% caustic solution is produced from the amalgam, and the mercury is recycled to the cell.

Energy requirements for the mercury cell include 3,712 kWh of power and 550 lb of steam/ton of chlorine (Volume XII, page 56). Steam is generated by natural gas and byproduct hydrogen. Approximately 0.72×10^6 Btu of fuel gas/ton of chlorine are required (Volume XII, page 56).

NO_x emissions from steam generation by natural gas and byproduct hydrogen are estimated to be 0.21 lb/ton of chlorine. NO_x emissions produced by a coal-fired power boiler are estimated to be 29.25 lb/ton of chlorine.

Summary

The emissions factor and total emissions for the baseline and alternative processes are presented in Table 21. The modified anodes and modified diaphragm options offer between a 5% to 16% yearly reduction in NO_x emissions from the base case process.

The mercury cell, however, is estimated to result in a 4% yearly increase from the base case because of the relatively larger power requirements.

TABLE 21. ESTIMATED NO_x EMISSIONS - CHLOR-ALKALI INDUSTRY
BASIS: NO ADD-ON TECHNOLOGY FOR NO_x CONTROL

Process	NO_x estimated emission factor (lb/ton of chlorine) Process	Power boiler	Total	Change from base case	NO_x emission (10^6 lb/yr) 1974	1989-1974
Base case: Graphite-anode diaphragm cell**	2.65	25.80	28.45	--	313	339
• Dimensionally stable anodes	2.30	24.83	27.13	- 1.32	--	323
• Expandable DSA	2.30	22.28	24.58	- 3.87	--	293
• Polymer-modified asbestos	2.30	22.62	24.92	- 3.53	--	297
• Polymer membrane	2.30	22.62	24.92	- 3.53	--	297
• Ion exchange membrane	0.52	23.24	23.76	- 4.69	--	283
• Mercury cell	0.21	29.25	29.46	+ 1.01	--	351

* Based on increment in production from 1974 to 1989 = 11.9×10^6 ton/year.

** Estimated 1974 emissions, based on the total emission factor of 28.45 lb of NO_x/ton of chlorine are $28.45 \times 11.0 \times 10^6 = 313 \times 10^6$ lb.

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